Study on Contamination of Perfluorinated Compounds (PFCs) in Water Environment and Industrial Wastewater in Thailand

by

Chinagarn Kunacheva

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Bangkok, Thailand

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Department of Urban and Environmental Engineering,
Graduate School of Engineering, Kyoto University, Japan

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Abstract

PFCs are used in a wide variety of industrial and commercial applications for more than 50 years. Among variation of PFCs, Perfluorooctane sulfonate (PFOS) (CF3(CF2)7SO3-) and perfluorooctanoic acid (PFOA) (CF3(CF2)6COO-) are the most dominant PFCs. In May 2009, PFOS, its salts and perfluorooctane sulfonyl fluoride (PFOSF) are designated as new Persistent Organic Compounds (POPs) which are resistant, bio-accumulating, and having potential of causing adverse effects to humans and environment (IISD, 2009). However, products containing PFCs are still being manufactured and used, which could be the main reason why they are still observed in the environment and biota (Berger *et al.*, 2004; Saito *et al.*, 2003; Sinclair *et al.*, 2004).

The study is focused on the PFCs contamination in water and industrial wastewater around the Central and Eastern Thailand, where is one of the major industrialized areas in the country. The samplings were conducted in major rivers, Chao Phraya, Bangpakong and Tachin River. PFCs were contaminated in all rivers. The average total PFCs were 15.10 ng/L, 18.29 ng/L and 7.40 ng/L in Chao Phraya, Bangpakong and Tachin River, respectively. PFOS and PFOA were the predominant PFCs in all samples. The total of 118.6 g/d PFOS and 323.6 g/d PFOA were released from the three rivers to the Gulf of Thailand. The survey was also conducted in small rivers, reservoirs, and coastal water around Eastern Thailand, where many industrial zones (IZ) are located. The geometric mean (GM) concentration of each PFC was ranged from 2.3 to 107.7 ng/L in small rivers, 2.2 to 212.2 ng/L in reservoirs, and 0.8 to 41.1 ng/L in coastal water samples. The higher PFCs contaminations were detected in the surface water around the industrial zones, where might be the sources of these compounds.

Field surveys were also conducted in ten industrial zones (IZ1 – IZ10) to identify the occurrences of PFCs from in industries. The recovery rates of PFCs in the samples indicated that the matrix interference or enhancement was an important problem in PFCs analysis. The elevated concentrations were detected in electronics, textile,

chemicals and glass making industries. Total PFCs concentrations in the influent of WWTP were ranged from 39.6 to 3,344.1 ng/L. Ten industrial zones released 188.41 g/d of PFCs. All of the treatment processes inside industrial zones were biological processes, which were reported that they were not effective to remove PFCs. The influence of industrial discharges was affected not only the rivers and reservoirs but also in the coastal water. The PFCs in rivers and reservoirs were discharged to the Gulf of Thailand, which is the important food source for Thai people and exports.

Due to the problems in industrial wastewater analysis, several optimizing options were applied in PFCs analytical method especially in Solid Phase Extraction (SPE) procedure. The combination of PresepC-Agri and Oasis®HLB was the better option for analyzing PFCs in water samples. The optimum flow rate for loading the samples was 5 mL/min. Methanol (2 mL) plus Acetronitrile (2 mL) was the effective way to elute PFCs from the cartridges. The specific solvent percentages to elute each PFCs were identified for both water and industrial wastewater samples. The matrix removal methods by using Envi-Carb and Ultrafilter were effective for different types of industrial wastewater samples.

PFCs were detected in surface waters, which are the sources of tap and drinking water for the people in Central and Eastern Thailand. The surveys were conducted in Bangkok city. Samples were collected from water treatment plants (WTPs), tap water, and drinking water. PFCs were detected in all tap water and drinking water samples. PFOS and PFOA concentrations in raw water of WTP were found 4.29 ng/L and 16.54 ng/L, respectively. The average PFOS and PFOA concentrations in tap water were detected 0.17 and 3.58 ng/L, respectively. The tap water results also showed that PFOS and PFOA concentrations were not similarly detected in all area in the city. PFOA were detected higher in the western area, while PFOS concentration was quite similar in all areas. Overall, it can be concluded that the current treatment processes were not completely remove PFCs. Nevertheless, PFCs in particulate phase were effectively removed by the primary sedimentation and rapid sand filtration.

Elevated PFCs were found in the industrial zones (IZ2 and IZ5). To understand the distribution and fate of PFCs during industrial wastewater process, PFCs mass flows were studied. Higher PFCs in adsorbed phase were detected only in activated sludge and some influent samples. In IZ2, PFOA loading in the dissolved phase increased after activated sludge process by 5%. There was no degradation of PFOA inside the polishing pond. The highest loading to the treatment plant was PFOS with the loading of 2,382 mg/d and 1,529 mg/d in dissolved and adsorbed phase, respectively. Unlike PFCAs that showed no removal in the treatment process, PFOS were decreased during the treatment processes with 36% in the activated sludge process and 36% in the polishing pond. The predominant in this IZ5 was PFOS. The increasing of PFOS was also found in this treatment plant dissimilar to IZ2. PFOS was increasing by 45% in dissolved phase and 47% in adsorbed phase. All of PFCs in this industrial zone were detected higher in the effluent, indicated that PFCs' precursors should be the major effects of this contamination.

Keyword

Perfluorinated compounds (PFCs), PFOS, PFOA, surface water, industrial wastewater, analysis method, tap water, mass flow

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Abbreviations

AC	activated carbon
AOPs	advanced oxidation processes
AS	activated sludge process
ASE	accelerated solvent extraction
Ave	average
DOC	dissolved organics carbon
ESI	electrospray ionization
GAC	granular activated carbon
GM	Geomean
IZ	Industrial Zone
LC	liquid chromatograph
LOD	limits of detection
LOQ	limits of quantification
MS/MS	tandem mass spectrometer
PFCs	perfluorochemicals
PFDA	perfluorodecanoic acid
PFDoA	perfluorododecanoic acid
PFHpA	perfluoroheptanoic acid
PFHxA	perfluorohexanoic acid
PFHxS	perfluorohexane sulfonate
PFNA	perfluorononanoic acid
PFOA	perfluorooctanoate
PFOS	perfluorooctane sulfonate
PFPA	perfluoropentanoic acid
PFUnA	perfluoroundecanoic acid
PET	Polyethylene terephthalate
POPs	persisted organic pollutants
PP	polypropylene

RO	reverse osmosis
SD	standard deviation
SPE	solid phase extraction
WTP	water treatment plant
WWTP	wastewater treatment plant

Chapter 1

Introduction

1.1 Research Background

Water is extremely essential to our life. Recently, water consumption is increasing continuously. One of the major problems is the limitation of water resources. Therefore, the uses of limited water resources efficiently become challenging issues. In addition, a problem nowadays is that many new chemicals have been generated and released to the water resources and one of the most concerned substances is persistent organic pollutants (POPs). POPs are chemical organic compounds which are resistant to environmental degradation (biological, chemical, and photolytic), existing in the environment for long-term periods, bio-accumulating through the food chain, and having potential of causing adverse effects to humans and environment (USEPA, 2006). Currently, one of the arising POPs is Perfluorinated compounds (PFCs).

Nowadays, PFCs are used in a wide variety of industrial and commercial applications. Due to oil, grease, water resistant properties, PFCs-related substances have been widely used in daily life such as carpets, leather, textile, paper and packaging, coating materials, cleaning products, pesticides and insecticides, and fire fighting foams (Keml, 2006; EUROPA, 2005). Among variation of PFCs, Perfluorooctane sulfonate (PFOS) ($CF_3(CF_2)_7SO_3^-$) and Perfluorooctanoic acid (PFOA) ($CF_3(CF_2)_6COO^-$) are the most concerned PFCs. In 2009, PFOS and related chemicals are selected as new POPs (IISD, 2009). Many PFCs-related regulations have been released to minimize PFCs contamination (EC, 2006, USEPA, 2006b). However, products containing PFCs are still being manufactured and used, which could be the main reason why they are still observed in the environment and biota (Berger *et al.*, 2004; Saito *et al.*, 2003).

Once released into the environment, these chemicals persist and are distributed throughout the global environment, found in surface waters and tap water in both developed and developing countries from around the world including U.S.A., Europe and Asia. (Hansen *et al.*, 2002; Sinclair *et al.*, 2004; Berger *et al.*, 2004; Lien *et al.*, 2006). In addition, these chemicals have been detected in livers, bladders and blood samples of human and many kinds of animal including, fish, birds, and marine mammals (IPEN, 2005; Renner, 2001; Giesy and Kannan, 2001). Furthermore, the recent researches found that PFOS is toxic to rats and monkeys (3M Company, 2003a, Renner, 2001).

The literature reported the PFCs contaminations from all over the world, especially in developed countries. Unfortunately, the study on PFCs contamination in developing countries was very limited. The survey of PFCs in developing countries like Thailand could give important information to understand worldwide actual condition on PFCs pollution. Prevedouros *et al.*, 2006 also indicated that industrial sectors are the major source of releasing PFCs into the surface water. The major industrialized area in Central and Eastern Thailand were selected as the target areas, where numerous national and multinational industries have been already established. The possibility of the presence of PFCs in this area is highly expected.

1.2 Research Objectives

Based on research background, the study focused on the PFCs contamination in water and industrial wastewater around the industrialized area. Occurrences of PFCs in surface water were evaluated and compared to other Asian cities. The industrial zones (IZ), where many industries located, are the possible sources of PFCs releasing to surface water. The surveys were conducted in ten industrial zones to identify the occurrences from industrial activities. Development of PFCs analysis in industrial wastewater samples was performed to further calculate the mass flow from central wastewater treatment plant in the industrial zones. Furthermore, the surface water is the source of tap water in the area. Performances of water treatment processes were

determined. The occurrences of PFCs in tap and drinking water in Bangkok city were also identified.

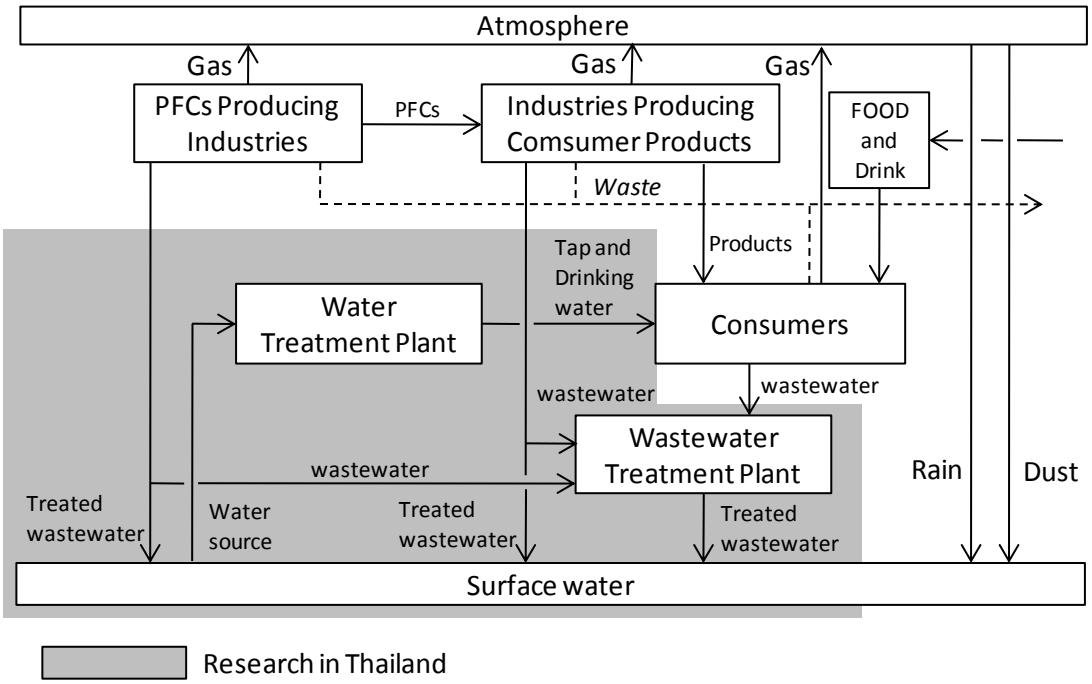


Figure 1.1 Scope of the study

Major objectives of the study are as follows:

1. To identify the occurrences of PFCs in surface water and to recognized the possible sources of PFCs contamination
2. To determine PFCs contaminations in industrial wastewater from industrial zones
3. To develop PFCs analysis method for industrial wastewater samples
4. To identify the occurrences of PFCs in water treatment plant, tap and drinking water in Bangkok, Thailand
5. To identify PFCs mass flows inside industrial wastewater plant

This dissertation consists of eight chapters (Figure 1.2). Overall contents are introduced by chapters as follows:

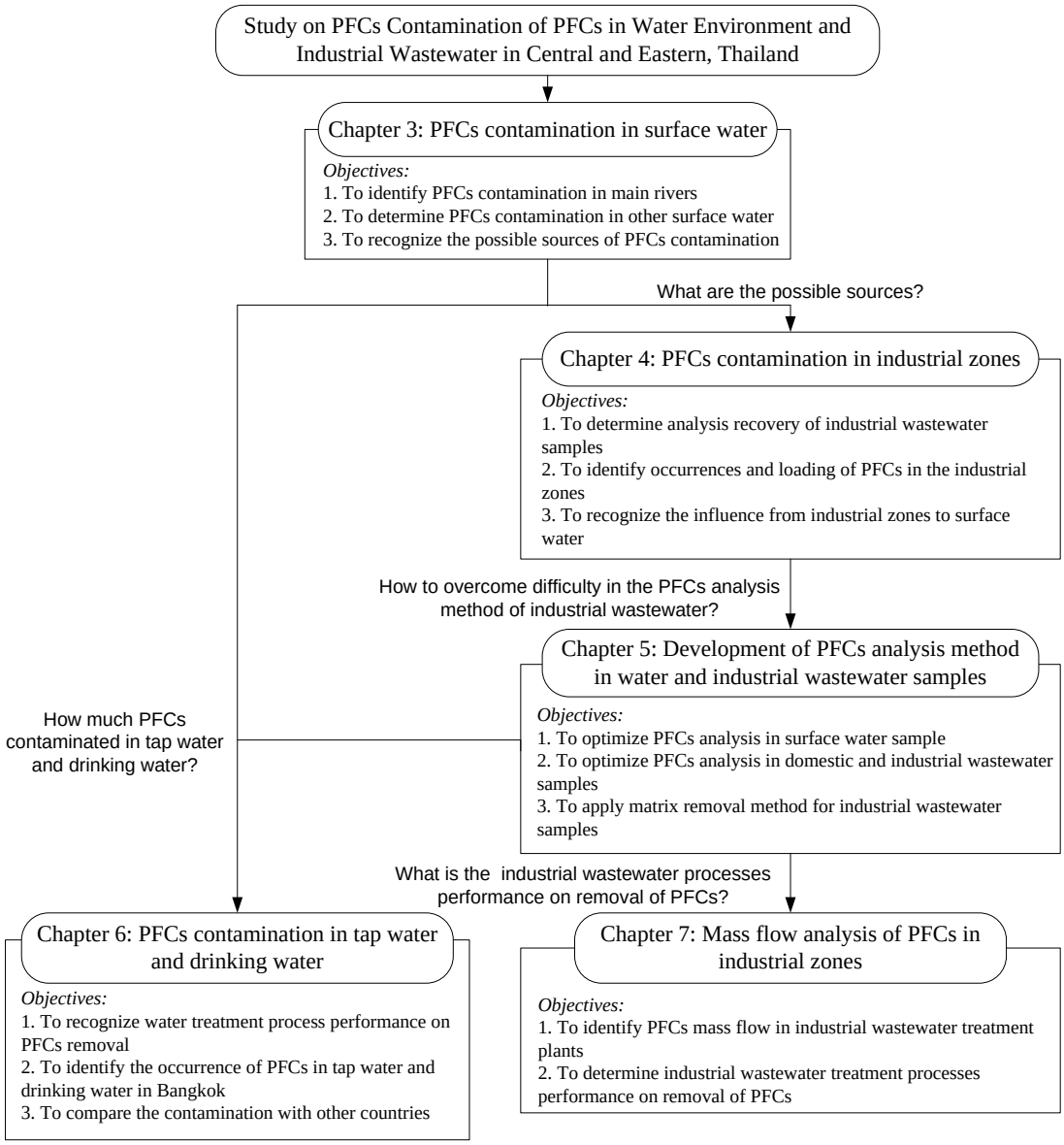


Figure 1.2 Frame work of the study

Chapter 1: gave a brief introduction of this research, including research background, objectives and dissertation structures.

Chapter 2: reviewed current available literature on PFCs, including their basic properties, analytical methods, occurrences and removal efficiency.

Chapter 3: identified the PFCs contamination in surface water and recognizing the possible sources of PFCs contamination.

Chapter 4: determined the conventional analysis recovery on analyzing PFCs in industrial wastewater. The occurrences of PFCs in industrial zones were recognized.

Influences of PFCs contamination from industrial wastewater to surface water were also determined in this chapter

Chapter 5: developed analysis method for industrial wastewater samples

Chapter 6: determined the water treatment process performance on removal of PFCs. Occurrences in tap water and drinking water were also identified in Bangkok city.

Chapter 7: identified PFCs mass flows inside wastewater treatment plant process.

Chapter 8: gave conclusions of this study and recommendations for further research.

To complete these objectives the sampling were conducted in Thailand as in Table 1.1.

Table 1.1 Summary of the samplings in Thailand

Time	Date	Place	Sampling Point	Number of Samples	Objective	Chapter
1st	2007/5/25	Industrial zone (IZ7)	12	24	Industrail Zone Contamination	4
2nd	2007/8/24	Industrial zones (IZ8 and IZ9)	17	34	Industrail Zone Contamination	4
3rd	2007/9/18	Industrial zone (IZ8)	11	22	Industrail Zone Contamination/ Method Development	4, 5
4th	2007/9/19	Chao Phraya River (1st)	19	38	River Contamination	3
5th	2007/12/6	Industrial zone (IZ1)	17	34	Industrail Zone Contamination	4
6th	2007/12/7	Bangpakong River	12	24	River Contamination	3
7th	2008/2/8	Industrial zones (IZ2 and IZ3)	22	44	Industrail Zone Contamination/ Method Development	4, 5
8th	2008/6/28	Industrial zones (IZ4 and IZ5)	13	52	Industrail Zone Contamination/ Method Development	4. 5
9th	2008/6/24	Chao Phraya River (2nd)	19	38	River Contamination	3
10th	2008/7/2	Eastern Thailand Surface water	12	24	River Contamination	3
11th	2008/8/22	Industrial zones (IZ2 and IZ3)	16	96	Industrail Zone Contamination/ Method Development	4, 5
12th	2008/8/29	Industrial zones (IZ5 and IZ6)	14	84	Industrail Zone Contamination/ Method Development	4, 5
13th	2008/8/4	Chao Phraya River (3rd)	19	38	River Contamination	3
14th	2008/10/30	Industrial zone (IZ10)	5	10	Industrail Zone Contamination	4
15th	2008/10/23	Tachin River	6	12	River Contamination	3
16th	2009/1/27	Water Treatment Plant (WBK and WSS), tap water, drinking water	22	44	Water Treatment Plant Performance/ Tap and Drinking water Contamination	6
17th	2009/1/28	Water Treatment Plant (WMS and WTB), tap water, drinking water	20	40	Water Treatment Plant Performance/ Tap and Drinking water Contamination	6
18th	2009/1/20	Industrial Zone (IZ2)	5	50	Industrial Zone Contamination/Mass Balance	7
19th	2009/1/22	Industrial Zone (IZ5)	5	50	Industrial Zone Contamination/Mass Balance	7
		Total	266	758		

Chapter 2

Literature Review

2.1 Introduction to Perfluorinated Compounds (PFCs)

Recently, protecting our fresh water resources has becomes very challenging due to growing water scarcity, increasing demand, and deterioration of water quality by polluting substances. Especially, contamination of water environment by new chemicals and organic micro pollutants is becoming very serious issue. POPs are the class of organic compounds that remain intact in the environment for long periods, resist photolytic, chemical and biological degradation, become widely distributed geographically, accumulate in the fatty tissue of living organisms and are toxic to humans and wildlife (USEPA, 2006). Compared with other pollutants the management of organic micro pollutants requires different approach than managing wastewater, eutrophication, or other pollution problems. The magnitude of problem becomes bigger when the type of pollutants is new and unique in characteristics.

Nowadays, one of the mostly concerned new types of organic micro pollutant is Perfluorinated Compounds (PFCs). Perfluorinated compounds (PFCs) have been synthesized and widely used in the industrial and commercial applications since the 1960s. Two major processes to synthesize PFCs are electrochemical fluorination and telomerization which hydrogen atoms in organics are substituted completely by fluorine atoms. PFOS ($CF_3(CF_2)_7SO_3^-$) and PFOA ($CF_3(CF_2)_6COO^-$) are the predominant PFCs. PFOS and PFOA are becoming new issues in environmental protection's perspective. These two chemicals are shown the properties in of POPs. In 2009, PFOS and related compounds were recognized as new POPs in Stockholm Convention.

Since PFOS has been applied in various products worldwide for the past 40 years and PFOA is still being manufactured and used, there are possibilities that these compounds

are released into the water environment through both point-source (industrial and sewage treatment plant) and non-point-source (surface run-off and atmospheric) discharges, bioaccumulated in the food chains and thus become a potential health risk to humans and animals. There are many kinds of Pefluorinated compounds. The PFCs in this study are shown in Table 2.1.

Table 2.1 Basic information of PFCs in this study

Compound	Fullname	Molecular weight	Chemical formula
PFPA	Perfluoropentanoic acid	263	$CF_3(CF_2)_3COO^-$
PFHxA	Perfluorohexanoic acid	313	$CF_3(CF_2)_4COO^-$
PFHpA	Perfluoroheptanoic acid	363	$CF_3(CF_2)_5COO^-$
PFOA	Perfluorooctanoic acid	413	$CF_3(CF_2)_6COO^-$
PFNA	Perfluorononanoic acid	463	$CF_3(CF_2)_7COO^-$
PFDA	Perfluorodecanoic acid	513	$CF_3(CF_2)_8COO^-$
PFUnA	Perfluoroundecanoic acid	563	$CF_3(CF_2)_9COO^-$
PFDoA	Perfluorododecanoic acid	613	$CF_3(CF_2)_{10}COO^-$
PFHxS	Perfluorohexane sulfonate	399	$CF_3(CF_2)_5SO_3^-$
PFOS	Perfluorooctane sulfonate	499	$CF_3(CF_2)_7SO_3^-$

2.1.1 Physico-Chemical Properties of PFOS and PFOA

The predominant PFCs are PFOS ($CF_3(CF_2)_7SO_3^-$) and PFOA ($CF_3(CF_2)_6COO^-$), which are fully fluorinated organic compounds which can be produced synthetically or through the degradation of other fluorochemical products. Due to soil, oil, grease, water resistant properties, PFOS-related substances have been widely used in daily life products such as carpets, leather, textile, paper and packaging, coating materials, and specialized products (Keml, 2006; EUROPA, 2005).

PFOS is an exceptionally stable compound in industrial applications and in the environment because of the effect of aggregate carbon–fluorine bonds. PFOS is a fluorosurfactant that lowers the surface tension of water more than that of hydrocarbon surfactants. The carboxylate group of PFOA is hydrophilic while the fluorocarbon chain is hydrophobic. PFOA is an ideal surfactant because it can lower the surface tension of

water more than hydrocarbon surfactants while possessing exceptional stability due to the presence of multiple carbon–fluorine bonds (Lemal, 2004). The stability of PFOA is desired industrially, but is a cause of environmental concern. PFOA is resistant to degradation by natural processes such as metabolism, hydrolysis, photolysis, or biodegradation making it persist in the environment (OECD, 2002).

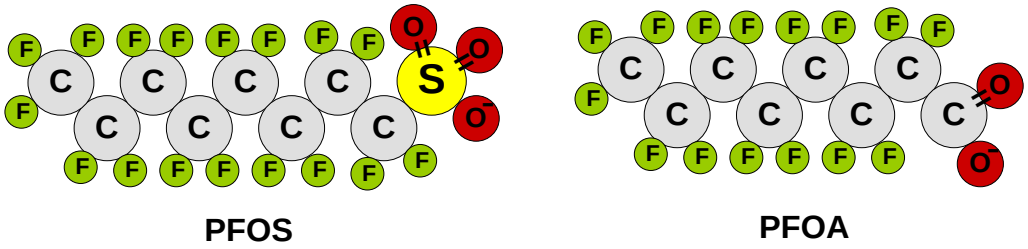


Figure 2.1 PFOS and PFOA chemical structure

Table 2.2 Physico-chemical properties of PFOS and PFOA

Properties	PFOA	PFOS
Molecular weight	414	500 (for acid)
Melting point	45-50^{o}C	>= 400^{o}C
Boiling point	189-192^{o}C (736 mmHg)	not calculable
Vapor pressure	10 mmHg (25^{o}C)	3.31x10^{-4} Pa (20^{o}C)
Solubility in pure water	3.4 g/L	570 mg/L (in pure water)
Air/water partition coefficient	not available	< 2x10^{-6}
pKa	2.5	not available
pH	2.6 (at 1g/L)	7-8 (for potassium salt of PFOS)

Source: OECD (2002) and USEPA (2002)

The characteristics of PFOS and PFOA, shown in Table 2.2, indicate that they are rather low in vapor pressure, highly soluble in water, and persistent in the environment. Therefore, most of the PFOS and PFOA discharged into a water body would probably remain in that medium, unless they are adsorbed onto particulate matter which would

eventually settle down to the sediment, or assimilated by organisms and enter the ecosystems through bioaccumulation in the food chains.

2.1.2 Production and Applications

Production of Perfluoroalkyl carboxylates began in 1947 using an electrochemical fluorination process. PFCs used in industries were mainly produced in processes of electro-chemical fluorination (ECF) and telomerization. Electro-chemical fluorination (ECF) was adopted by 3M Company to produce organofluorine chemicals. Telomerization process was developed by DuPont. The related products based on telomerization are manufactured by a number of companies, including DuPont, Asahi Glass, Atofina, Clariant, and Daikin (Lange *et al.*, 2006).

Prevedouros *et al*. (2006) estimated the global historical production of perfluorocaboxylates (PFCAs) up to 2006 to be 4,400 – 8,000 tonnes, while the total global (both direct and indirect) emissions to the environment were 3,200 – 7,300 tonnes. The majority of these emissions came from the fluoropolymer manufacturing production. Among the various forms of PFCAs, PFOA is the most detected compound in the water environment and biota. The production of PFOS-related chemicals is in the U.S.A., Europe and Japan. In 2000, approximately 4,500 tonnes of PFOS-related chemicals have been produced annually. The major global producer of PFOS, 3M Company, completed phasing out the production in 2002 (3M Company, 2000). PFCs are used in a wide variety of industrial and commercial applications. They have been used for producing daily life products such as carpets, leather, textile, paper and packaging, coating materials, cleaning products, pesticides, insecticides, and fire fighting foams (EC, 2006). Specific applications of PFOS include surface treatment, semiconductor industry, paper protection, and performance chemicals, while PFOA is used as emulsifier and surfactant (OECD, 2002).

2.1.3 Hazard of PFCs

PFOS is persistent in the environment and has been shown to bioaccumulation in fish and also has been detected in a number of species of wildlife, including marine mammals. Due to its properties (persistent, presence in the environment and bioaccumulation potential), indicating cause of concern. The toxicity of PFOS has been studied for many years.

PFOS and PFOA have been detected in livers, bladders and blood samples of human and many kinds of animal including, fish, birds, and marine mammals (IPEN, 2005; Renner, 2001). Animals in the higher food chain such as mink and bald eagles (fish-eating animals) contained higher concentrations of PFOS representing bio-accumulative properties (Giesy and Kannan, 2001). PFOS has been shown to be toxic in rats and rabbits in the laboratory (3M Company, 2003a; Renner, 2001). A 2-year bioassay in rats has shown that exposure to PFOS results in hepatocellular adenomas and thyroid follicular cell adenomas (OECD, 2002). The lowest observed adverse effect level (LOAEL) was 0.4 mg/kg bw/day and the no observed adverse effect level (NOAEL) of PFOS was estimated to be 0.1 mg/kg bw/day (OECD, 2002). Nevertheless, a PFOS risk assessment to human was not yet understood.

2.1.4 Regulations Related with PFCs

Table 2.3 shows timeline of important events related with PFCs invention, development, concerns, scientific activities and governmental policies. The PFCs was invented 70 years ago. DuPont is the first company to introduced Teflon to the world in 1950s. Although PFCs were detected in human blood in 1968 and in drinking water in 1984, the problem of these chemicals' were not concerned till the year 2000.

3M Company is the first company that concerning about the environmental impact of PFOS. The company releases an agreement to phase out their PFOS usage in 2000.

Since then, the organizations such as US EPA and OECD have been focused on these harmful chemicals. Besides, many literatures about the detection of PFCs especially PFOS and PFOA were published from that period.

Table 2.3 Timeline of important action related with PFCs

Year	Organization	Actions
1938		Dr. Roy J. Plunkett discovers Teflon by accident
1949	DuPont	Introduces Teflon
1956	3M Company	Starts selling Scotchgard Protector
1968		Dr. Taves found two forms of fluoride in human serum
1978	3M Company	Detects PFOS and PFOA in blood of workers
1981	3M Company	Eye defect found in rat study
1984	DuPont	DuPont found PFOA in local drinking water
1986	DuPont	Begin selling Teflon-based Stainmaster
1999	DuPont	Dump 55,000 pounds of PFOA into Ohio River
2000	DuPont	Release 31,250 pounds of PFOA into air
2000	3M Company	Phase out their usage of PFOS
2002	US EPA	Begins review of data that links C8 to health problems
2002	OECD	Issue hazard assessment of PFOS and its salts
2003	Japan EPA	Starts 1st Survey on surface water, aquatic life and sediment
2003	3M Company	Replaces C8 in Scotchgard with a C4 chemical
2003	Japan EPA	Detect high PFOA in Kinki area including Yodo River Basin
2004	US EPA	Start own scientific studies on C8 chemical
2004	Canada	Issue exposure to PFOS and related precursors by Health Canada
2005	US EPA	Issue risk assessment of PFOA-related chemicals on human health
2006	UNEP	Propose PFOS as POPs candidate to Stockholm Convention
2006	US EPA	Initiate 2010/15 PFOA stewardship program
2006	EC	Release Directive 2006/122/EC
2007	MDH	Set health based value of PFOS and PFOA
2007	New Jersey	Release PFOA guidance in drinking water
2009	UNEP	Perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride were selected as new POPs

In 2006, USEPA released the Initiate 2010/15 PFOA stewardship program in 2006. The purpose of this program is that eight major PFCs producers, including 3M Company and Daikin, have to phase out their usage of PFOA by 95% in 2010 (USEPA, 2006). European Commission also focuses on this issue. The Directive 2006/122/EC released in December 2006 for prohibiting selling of PFOS containing products in Europe (EC, 2006). PFOS and related compounds were proposed as new POPs candidate in

Stockholm Convention and were registered in Annex B in 2009. The convention decided to restrict the production of PFOS and related compounds only for purposes in photo-imaging, fire fighting foam and insect baits for leaf-cutting ants; and specific exemptions including, metal plating, leather and apparel, textiles and upholstery, paper and packaging, and rubber and plastics (IISD, 2009).

Unfortunately, exposure criteria of PFCs for human health were still in consideration and there was no agreement recently. One reason referred to the unreliable original data for assessment, and the other reason was related with the negotiation between government and industries. However, there are some criteria have been released in United States.

Minnesota Department of Health recommended 7 μg/L in drinking water as the safe level of PFOA for human health in 2002, and revised it to be 0.5 μg/L in 2007 (MDH, 2007). Other PFCs were also included in the criteria as 0.3 μg/L for PFOS, 1 μg/L for perfluorocarboxylates (PFCA) (C_4, C_6), and 0.6 μg/L for perfluoroalkyl sulfonates (PFAS) (C_4, C_6), because all of them have been detected in local surface water and drinking water. North California Division of Water Quality proposed 2 μg/L of PFOA to be temporary maximum allowable concentration, which was calculated by reference dose of 0.3 μg/kg-day (NC DWQ, 2006). New Jersey also released the PFOA guidance in drinking water to be 40 ng/L (New Jersey Department of Environmental Protection, 2009).

2.2 Analytical Method of PFCs

2.2.1 Sampling and Storage of Samples

Sampling and storage of samples for PFCs analysis are significant because during these stages losses and contamination can easily occur. Rising sampling bottles with solvents such as de-ionized water, acetone, methanol, or other solvent were needed to pre-clean prior to sampling (Martin *et al*., 2004; Yamashita *et al*., 2005). Yamashita *et al*. (2004)

noted that PFOA was found in new polypropylene sampling bottles. Therefore, the cleaning process before sampling is important especially for research targeting low concentrations in water samples (ng/L). Furthermore, samples should be analyzed directly after samplings, however, for long term storage, freezing at - 20ºC is preferred (Leeuwen and de Boer, 2007).

2.2.2 Pretreatment Methods for PFCs analysis

The aims of extraction and clean up are (1) to separate the preferred analytes from the unwanted ones, (2) to concentrate the analytes of interest, and (3) to purify the extract prior to instrumental determination. Before extraction of PFCs from the samples, pre-treatment procedures were required to remove matrix constituents that will cause interference or enhancement of the instrumental determination. Several pre-treatment options for water, sediment, and sludge samples are listed in Figure 2.2 (modified from Leeuwen and de Boer, 2007).

In most environmental samples, PFCs were found in ng/L or pg/L levels, which are requiring a procedure to increase the concentration level for instrumental determination. Both liquid-liquid extraction (LLE) and solid phase extraction (SPE) are suitable for this purpose as reported by Yamashita *et al*. (2004), Gonzalez-Barreiro *et al*. (2006), and Taniyasu *et al*. (2005). Different SPE cartridges have been used, including PresepC-Agri (C18), Oasis®HLB, and Oasis®WAX. In general, the performance of Oasis®WAX and Oasis®HLB was comparable. Recoveries was good for most PFCs (70-100%). However, the recoveries for the long chain perfluorinated carboxylates ($\geq C_{11}$) were <70% for both column types (Taniyasu *et al*., 2005). Yamashita *et al*., 2004 developed a very sensitive SPE method (pg/L level) for seven perfluorinated sulfonates based on OasisHLB for sea water samples.

Recently, new extraction and clean-up methods have been introduced that enable the analysis in various samples including sediments, soil, and sludge samples. Powley *et al*. (2005) developed a virtually matrix-effect free Liquid-solid extraction (LSE) and cleanup method for soil, sediment, and sludge samples. PFCs were extracted by

methanol in basic condition. The sample was shaking for 30 min. The extract was neutralized by HCl. After using active carbon (Supelclean Envi-Carb), the extract was ready for analysis. The recovery was good 75-120% for C_6 to C_{14} PFCAs.

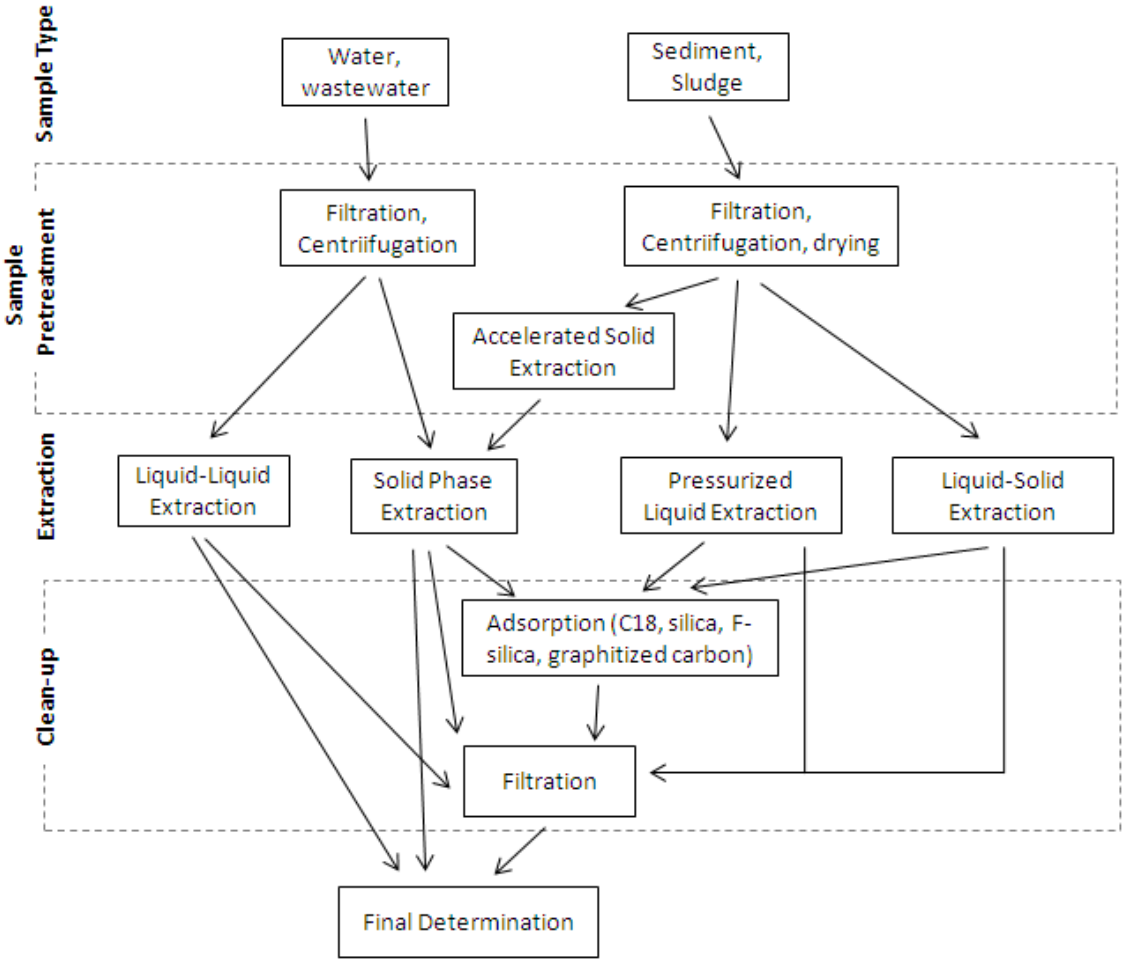


Figure 2.2 Extraction and cleanup methods for analysis of PFCs in water, wastewater, sediment, and sludge samples (modified from Leeuwen and de Boer, 2007)

2.2.3 Analysis of PFCs by HPLC-ESI-MS/MS

The development of trace chemical analysis by using liquid chromatography coupled with mass spectrometer has been achieved as low as ng and pg level. ESI was found the best interface for all LC-MS systems (Kuehl and Rozynov, 2003; Martin *et al.*, 2004). Different types of mass spectrometer were tried for PFCs analysis. Triple

quadrupole MS was most often applied in PFCs analysis. Although LC-MS showed satisfied performances on PFC analysis, strong interferences might occur in analysis as matrix effect. Therefore, tandem MS/MS was required to quantify environmental samples for its higher selectivity (Field *et al*., 2005).

Reverse-phase C18 column was most popular for LC separation. Compatible guard column can effectively extend life of LC column, and was usually applied to protect LC column. Optimum LC mobile phase for polar PFCs was water and methanol, with pH buffer of ammonium acetate in different concentrations. Acetonitrile was also applied in some studies. Because methanol can enhance ionization (Maestri *et al*., 2006), application of *ultrapure* water/methanol as mobile phase was helpful to overcome strong ionization suppression which often happened in environmental sample analysis. Improvement of matrix effect control could be achieved by applying new extraction materials (Zhao *et al*., 2007), by refined cleanup process (Schröder, 2003; Powley *et al*., 2005), or by directly elimination of pretreatment steps in large-volume-injection method (Schultz *et al*., 2006). More information about PFCs analytical quality control was available in some critic reviews (Martin *et al*., 2004a; de Voogt and Saez, 2006; Marta *et al*., 2006; Leeuwen and de Boer, 2007).

2.3 PFCs Occurrences in Environment, Human, and Biota

2.3.1 Occurrences of PFCs in Surface Water

Once PFOS and PFOA are released into the environment, these chemicals persist and are distributed throughout the global environment, they are found in surface waters and tap water in both developed and developing countries from around the world including North America, Europe and Asia. In U.S.A., Sinclair *et al.* (2004) reported that PFOS and PFOA were found in Michigan surface waters. The highest concentration of PFOS and PFOA were 29 ng/L and 36 ng/L respectively where several paper mills were located. Sinclair *et al.* (2006) found that PFOS and PFOA concentrations in surface water of New York State to be 0.8 – 30 ng/L and 10 – 173 ng/L, respectively.

Especially in Lake Onondaga, PFOS concentration was remarkably high around 198 – 1090 ng/L because of discharging from the industries.

In Northern Europe, Berger *et al.* (2004) found that five different sources of water were containing PFOA; 5.2 ng/L in seawater, 7.8 ng/L in lake water, 13.1 ng/L in rainwater, 20.5 ng/L in sewage effluent and 297 ng/L in landfill leachate. PFOS was not dominant in the aqueous samples average less than 1 ng/L for sea, lake and rainwater and 12.7 and 65.8 ng/L for sewage and landfill effluent, respectively.

Japan is the first country in Asia concerning about PFOS and PFOA contamination in the environment. Taniyasu *et al.* (2002), who wrote the first report on PFOS contamination of the water environment in Japan, found that the Tokyo bay water containing the highest PFOS concentration of 59 ng/L (Ave. 26 ng/L). Lower PFOS concentrations were detected Osaka bay (12 ng/L), Ariake bay (9 ng/L), Lake Biwa (7.4 ng/L), and Seto inland sea (< 4.3 ng/L). A later survey conducted by Saito *et al.* (2004) found the contamination of PFOS and PFOA in surface water at many locations in Japan which are in the ranges of 0.89 – 3.69 ng/L and 0.97 – 21.5 ng/L, respectively. The highest PFOA concentration of 21.5 ng/L was found in a surface water of Kinki area, western Japan. The contamination source was a sewage treatment plant that was estimated to discharge about 18 kg of PFOA per day into a nearby Kanzaki river which flows into the Osaka bay.

Besides, Lien (2007) found that some sewage treatment plants discharged their treated effluents containing PFOS and PFOA into the Yodo River which also flows into the Osaka bay. The PFOS and PFOA concentrations of these effluents were in the ranges of 3 – 76 ng/L and 25 – 922 ng/L, respectively. Therefore, the amounts of PFOS and PFOA discharges into the Osaka bay through the Yodo River were estimated to be 64 and 375 g/d, respectively. Surface water in other Asian countries was also reported by Tanaka *et al*. (2008) and Kunacheva *et al.*, (2009). Figure 2.3 shows PFOS and PFOA concentration in Asian countries.

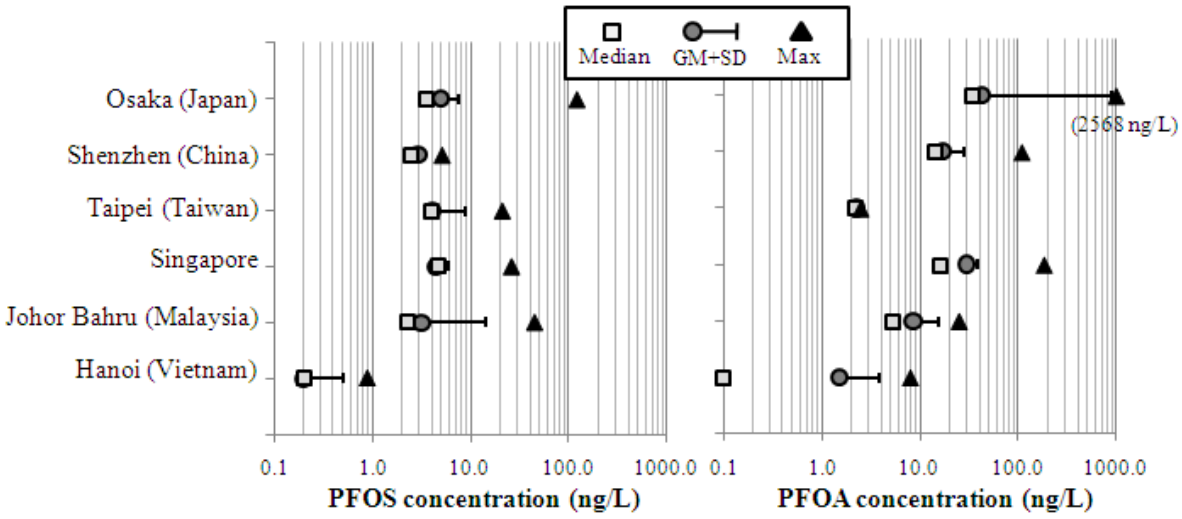


Figure 2.3 PFOS and PFOA concentrations in surface water in Asian countries

2.3.2 Occurrences of PFCs in Tap Water

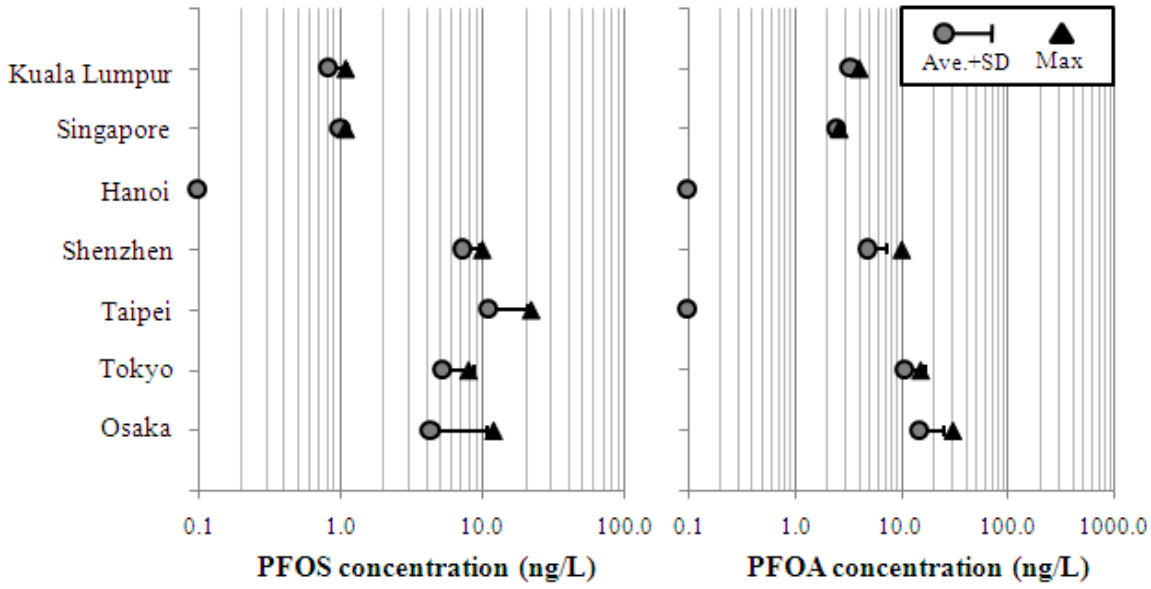


Figure 2.4 PFOS and PFOA concentrations in tap water in Asian countries

Tap water in several cities in Japan also were found that containing PFOS and PFOA in the ranges of Non-Detectable (ND) – 6.8 ng/L and 0.3 – 37.5 ng/L, respectively (Lien, 2007). Not only in Japan, tap water in some cities from other countries including Canada, China, Malaysia, Sweden, Thailand and Vietnam were also found to contain

PFOS and PFOA in the ranges of ND – 13.2 ng/L and ND – 109 ng/L, respectively (Tanaka *et al*., 2008). The summary of PFOS and PFOA concentrations in tap water in Asian cities were summarized in Figure 2.4 Currently, there is no standard of guideline value of PFOS and PFOA. However, New Jersey Department of Environmental Protection (2009) reported the guideline PFOA concentration in tap water is 40 ng/L.

2.3.3 Occurrences of PFCs in Oceanic Water

Samplings were conducted around coastal area, where densely populated and industrialized countries (Saito *et al*., 2004; Yamashita *et al*., 2005; Caliebe *et al*., 2004). Discharges of major rivers and sewage treatment plants would be significant for most of these sites. Reported PFOA levels in coastal waters generally varied between 0.2 and 20 ng/L, the highest concentration was detected 450 ng/L in South East Asia samples. PFOA concentrations in open ocean samples in surface and also deep water have been reported (Yamashita *et al*., 2005; Sinclair *et al*., 2004). The lower level of PFOA concentration was detected varying from 0.015 to 0.5 ng/L. A deep ocean water PFOA concentration of 69 pg/L (1000 – 4400m) has been reported (Yamashita *et al*., 2005).

2.3.4 Occurrence of PFCs in Wastewater

Due to high consumption of fluoropolymer and telomer-alcohols in the industries, industrial discharge is considered to be a major source of PFOS and PFOA contaminations. Tang *et al.* (2006) reported that wastewater from the semiconductor industry contained PFOS around 1,650 mg/L, much higher than its solubility in water (550 mg/L, Table 2.2) due to the fact that this wastewater contained about 5% isopropyl alcohol added to enhance PFOS solubility. Currently, development of a PFOS substitute could take several years away. Hence, some industries would continue to use PFOS in their production processes for many years to come.

PFOS and PFOA were detected not only in industrial wastewater but also in domestic wastewater. PFCs contaminations in domestic wastewater have been reported from many countries. In U.S.A., Boulanger *et al*. (2005) reported the PFOS and PFOA

contaminations in domestic wastewater in Iowa, containing 26 ng/L and 22 ng/L, respectively. The similar PFCs levels were also found in the effluent of municipal wastewater treatment plant in Pacific Northwest. The range of PFOS and PFOA were 12 – 27 ng/L and 7 – 16 ng/L, respectively (Schultz *et al*., 2006). Higher PFCs concentrations were detected in six WWTPs in New York State. PFOS and PFOA concentrations were varied 4 – 68 ng/L and 58 – 1,050 ng/L, respectively (Sinclair and Kannan, 2006).

WWTPs received wastewater from only domestic and commercial activities. This suggests that PFCs can occur at hundreds of ng/L concentrations without influence from fluorochemical manufacture or industry. The study on PFCs contaminations in domestic wastewater also conducted in Glatt Valley, Watershed, Switzerland. Huset *et al*. (2008) reported the PFCs concentrations in influents and effluents from seven WWTPs. PFOS and PFOA were ranged 18 – 449 ng/L and 5 – 9 ng/L, respectively in the influents, and 16 – 303 ng/L and 12 – 35 ng/L in the effluents. The results show that PFOS and PFOA were not removed efficiently in all seven WWTPs and contaminated to the water environment downstream.

In Asia, the PFCs contaminations in wastewater were reported from Japan and Singapore. Murakami *et al*. (2009) conducted samplings in WWTPs to collect wastewater influents and secondary effluents in Kanto region, Japan. PFOS, PFOA, and PFNA concentrations were 14 – 336 ng/L, 14 – 41 ng/L, and 13 – 70 ng/L in the influents and 42 – 635 ng/L, 10 – 68 ng/L, and 17 – 94 ng/L, respectively. PFCs concentrations in the effluents were higher than in the influents, which are comparable to other studies in Japan (Qiu *et al*., 2007) and other countries (Schultz *et al*., 2006; Sinclair and Kannan, 2006). This is probably because PFCs are produced through biodegradation of precursors. In Singapore, Yu *et al*., 2009 reported PFOS and PFOA concentrations from two WWTPs, which receive wastewaters consisting of 95% domestic wastewater and 5% industrial and commercial wastewater. Due to seasonal variation, the range of PFOS and PFOA concentrations were 11 – 461 ng/L and 16 – 1057 ng/L, respectively.

2.3.5 Occurrence of PFCs in Human and Biota

Literatures have been reported the PFCs contamination in biota. Taniyasu *et al*. (2002) found the presence of PFOS in blood and liver samples of fish collected from several places in Japan at concentrations of 2 - 834 ng/mL. The highest mean PFOS concentration of 345 ng/mL was in the fish blood collected from Lake Biwa, followed by those collected from Tokyo bay (172 ng/mL), Osaka bay (100 ng/mL), Seto inland sea (29 ng/mL), Ariake bay (28 ng/mL) and Okinawa (10 ng/mL).

In U.S.A., PFOS was found in all liver samples of fish and birds collected from New York State at concentrations of 9 - 315 and 11 - 882 ng/g, respectively (Sinclair *et al*. 2006). Giesy and Kannan (2001) was conducted a survey found PFOS to be distributed widely in animal tissues, even in such remote locations in the Arctic and North Pacific Oceans, although those from the industrialized areas had greater PFOS concentrations than those from the less populated regions. PFOS were detected PFOS in the livers of minks from the U.S.A., containing 970 - 3680 ng/g higher than the livers of some Alaskan polar bears were found to contain 180 - 680 ng/g.

PFCs were also found in human blood samples. Literatures reported the concentrations of PFOS in human blood samples from different countries shows the levels of PFOS in whole blood to range from 2 to 20 ng/mL, while the concentrations in sera ranged from 4 to 1656 ng/mL (Kannan *et al*., 2004). The summary of PFOS concentration in human blood samples were shown in Table 2.4. According to Saito *et al*. (2004), tap water consumption was considered as a source of PFOA intake for people living in Osaka, Japan. Consumption of fish contaminated with these compounds could be another source of PFOS and PFOA intake. Other sources of PFOS and PFOA intake by human could be through consumption of contaminated foods and inhalation of air or even house dust as PFCs concentrations reported by Strynar *et al*. (2008). However, the current report from Olsen *et al*. (2008) was found that PFOS concentration in human blood samples were decreasing during the past few years. The report was found that concentrations of PFOS, PFOA, and PFHxS from 2001 to 2006 were declined 60%, 25%, and 30%, respectively.

Table 2.4 Concentration of PFOS (ng/ml) in human blood from different countries

Country	Number of sample	Mean	Range	Note	Reference
USA (Michigan, Kentucky and New York)	175	49.5	<1.3-164	Sera	Kannan *et al*. 2004
Colombia	56	8.2	4.6-14		
Brazil	27	12.1	4.3-35		
Italy	50	4.3	<1-10.3		
Poland	25	44.3	16-116		
India	45	2.0	<1-10.3		
Malaysia	23	12.4	6.2-18.8		
Korea	50	21.1	3.0-92		
Japan	38	17.1	4.1-40.3		
USA, Atlanta	20	NA	3.6-164	Sera	Kuklenyik *et al*. 2004
USA	645	34.9	<4.3-1656	Sera	Olsen *et al*. 2003
Japan	26	8.1	2.0-20.2	Whole blood	Masunaga *et al*. 2003
Japan	10	9	2.4-14	Whole blood	Taniyasu *et al*. 2003
Sweden	66	18.2	1.7-37	Whole blood	Karrman *et al*. 2004
USA	600	16.9	<2.5-77.9	Sera	Olsen *et al*. 2008

2.4 PFCs Treatment

2.4.1 Conventional Treatment Processes on Removal of PFCs

There are many studies published about the performance of conventional water and wastewater treatment plant to remove or degrade PFCs. A survey in ten WWTPs in United States showed no removal of PFOS except one WWTP with influent as high as 400 μg/L. PFOA in the effluent of seven WWTPs was increased by 10 - 100% of influent which contained 16 - 49 μg/L PFOS (Schultz *et al.*, 2006). Surveys of WWTPs in Iowa State also showed no removal of PFOS and PFOA, as well as other PFCs (Boulanger *et al.*, 2005 and Sinclair and Kannan, 2006).

Studies in WWTPs in Japan obtained similar results of ineffective to remove PFOA and PFOS by activated sludge process (Nozoe *et al.*, 2006). It can be conclude that the existing conventional activated sludge process might be ineffective to remove PFOS or PFOA, and certain amount of PFCs was discharged from WWTPs to environment. Most studies, only the influent and effluent were analyzed to estimate overall process performance. However, there was only one study which estimated performances of individual facilities in activated sludge process to reveal the interesting vision of PFCs behavior inside WWTP (Schultz *et al.*, 2006).

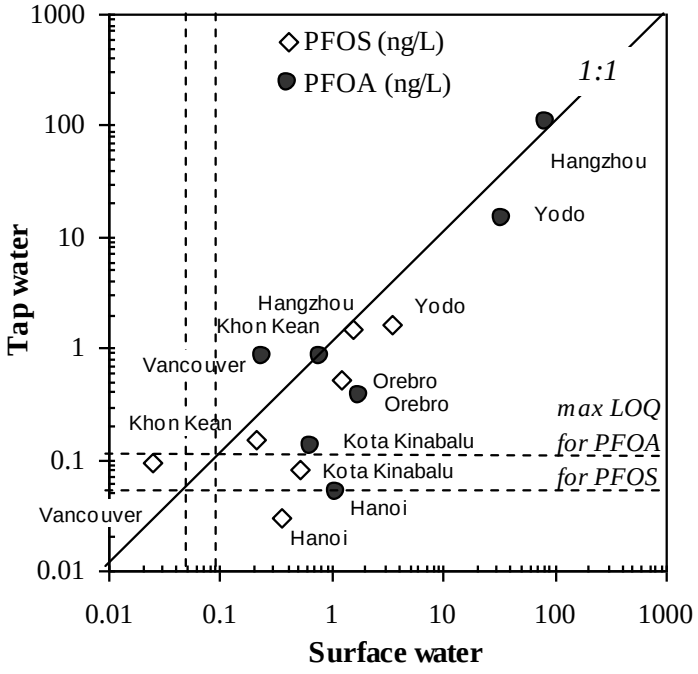


Figure 2.5 Mean concentrations of PFOS and PFOA in tap water against those in surrounding surface water (Lien *et al*. 2006)

In water treatment plant, the study of PFCs removal during the processes is limited. However, there is one study that can be roughly identifying the performance of the water treatment plant. Lien *et al.* (2006) identified the PFOS and PFOA concentration in tap water and surface water in the same area in many countries (Figure 2.5). The concentrations of PFOS and PFOA in 11 places are not much different between surface

and tap water in most samples. This result can be explained that the conventional water treatment process is not effective to treat PFCs.

2.4.2 Advanced Processes on Removal of PFCs

Advanced processes which have a possibility effectively to remove PFCs are membranes (Nano Filtration and Reverse Osmosis), activated carbon (Granular Activated Carbon and Powder Activated Carbon), Ion-Exchange, Ultraviolet Radiation and other Advanced Oxidation Process (AOP).

Membrane

The first study about PFOS removal by membrane process was used Reverse Osmosis (RO) membrane. Tank *et al.* (2006) applied four types of RO membrane in this study. The results indicated that PFOS can be efficiently rejected by all type of commercially available RO membranes over a wide range of feed concentrations from 0.5 – 1600 mg/L. All processes performances were above 99%. Consequently, RO membrane application seems to be an effective technology for removing PFOS from waste water.

Another research, which using Microfiltration (MF) and Nanofiltration (NF) membrane to remove PFOS, was done by Bureau of Water Works, Tokyo (2007). In this study, raw water of a water treatment plant containing PFOS (30 ng/L) and PFOA (8 ng/L) was used as feed water in this study. PFOS and PFOA in raw water cannot be removed by using MF membrane with nominal pore size 0.1 μm, but can be removed by using NF-150 and NF-65. Because the molecular weight of PFOS and PFOA is 499 and 413 respectively, the NF membranes with MWCO 150 and 65 can thoroughly remove PFOS and PFOA. The result shows that PFOS and PFOA can be removed by using membrane process and through appropriate selection of the MWCO of the membrane.

Activated Carbon

Activated Carbon is often applied to remove pollutants such as odor and color for drinking water purification and ground water remediation. There are two kinds of activated carbon, Powder Activated Carbon (PAC) and Granular Activated Carbon (GAC). Laboratory studies showed effective removal of PFOA by carbon adsorption (Schaefer, 2006). Industrial application of GAC column by 3M Company also confirmed the efficiency of adsorption.

Another lab-scale study was done by using PAC (Bureau of Water Works, Tokyo, 2007). Normal solution of PFOS and PFOA was to a raw water of a water treatment plant (1 µg/L). The raw water of this plant contains about 30 ng/L PFOS and 10 ng/L PFOA. By using a jar test experiment, PAC was added in the range of 0 – 100 mg/L in contact time 15 minutes. Figure 4 shows the results of the experiment. The removal performances were due to the PAC dosage, 80 – 90% removal of PFOS and PFOA can be obtained with 20 mg/L PAC and completely eliminated by using 50 mg/L or more. Nevertheless, in the real scale application, the results of environmental monitoring revealed strong correlations between PFC concentrations in surface and in drinking water, indicating ineffective removal by current water treatment process including GAC filters (Skutlarek *et al.*, 2006).

Ion-Exchange

Ion-Exchange resin is a practical process to use in the industrial recycling process and water purification. This process is also possible to apply in municipal WWTPs. Lampert *et al.* (2007) developed an initial study, a batch experiment comparing six Ion-Exchange resins (U.S. Filter). The initial concentration of PFOS and PFOA were 950 mg/L and 4,320 mg/L, respectively.

After that, a further study was done to identify the performance of resin type A-714 with the contact time 1, 5, 25 hours. The result was illustrated in Table 5. Ion-exchange resin A-714 column could concentrate PFOS and PFOA from wastewater by removal

efficiency of 99.5% and 92%, respectively in 5 hours, which was much higher than GAC adsorption. However, the detection level of PFOS and PFOA in environmental water (ng/L) is much lower than the initial concentration of this experiment (mg/L). The further study should focus on the removal rate of Ion-exchange in the trace level.

Ultraviolet Radiation

Ultraviolet (UV) is usually applied in disinfection step in water and wastewater treatment process. This process is effectively to decompose bacteria and virus. Hori, *et al.* (2004) applied a UV photolysis to decompose PFCAs. Direct photolysis (220-240nm) was able to completely degrade 560 mg/L PFCAs, although one early research claimed that no removal of PFOA was observed under either direct or indirect photolysis (Hatfield, 2001). UV process by using shorter wave length can generate higher energy photons and result in higher removal efficiency. Direct UV irradiation at 185 nm mercury lamp or 172 nm xenon quasi molecular laser light was found to be able to completely degrade some kinds of PFC (Zhang *et al*., 2005).

Advanced Oxidation Processes (AOP)

Advanced oxidation processes (AOPs), refers to chemical treatment procedures designed for removing organic and inorganic compounds in wastewater by oxidation. Contaminants are oxidized by these common processes include O_3/H_2O_2, O_3/UV and UV/H_2O_2. UV/TiO_2 process are also effective to specific wastewater (Gottschalk *et al.*, 2000). However, Schröder and Meesters (2005) identified that AOPs such as O_3, O_3/UV, O_3/H_2O_2 and H_2O_2/Fe^{2+} were unable to decompose PFOS in normal condition, but able to degrade PFOS precursors and partially fluorinated polymers effectively.

Chapter 3

Perfluorinated Compounds Contamination in Surface Water, Thailand

3.1 Introduction

PFCs are used in a wide variety of industrial and commercial applications. They have been used for producing daily life products such as carpets, leather, textile, paper and packaging, coating materials, cleaning products, pesticides, insecticides, and fire fighting foams. Among variation of PFCs, Perfluorooctane sulfonate (PFOS) ($CF_3(CF_2)_7SO_3^-$) and Perfluorooctanoic acid (PFOA) ($CF_3(CF_2)_6COO^-$) are the most concerned PFCs. Currently, these chemicals are labeled as new Persistent Organic Compounds (POPs) which are resistant, bio-accumulating, and having potential of causing adverse effects to humans and environment (USEPA, 2006a). As a result, many PFCs-related regulations have been released to minimize PFCs contamination (EC, 2006; USEPA, 2006b). However, products containing PFCs are still being manufactured and used, which could be the main reason why they are still observed in the environment and biota (Berger *et al*., 2004; Saito *et al*., 2003; Sinclair *et al*., 2004). The literature reported the PFCs contaminations from all over the world, especially in developed countries. Unfortunately, the study on PFCs contamination in developing countries was very limited. The survey of PFCs in developing countries like Thailand could give important information to understand worldwide actual condition on PFCs pollution.

Prevedouros *et al*., 2006 also indicated that industrial sectors are the major source of releasing PFCs into the surface water. The major industrialized area in Central and Eastern Thailand were selected as the target areas, where numerous national and multinational industries have been already established. The possibility of the presence of PFCs in this area is highly expected.

3.2 Objectives

The purposes of this field study were (1) to identify the contamination of PFCs in major rivers in Central and Eastern Thailand, (2) to determine PFCs contamination in small rivers, reservoirs, and coastal water, (3) to recognize the possible sources of PFCs contamination, and (4) to compare the contamination level with other countries.

3.3 Sampling Locations

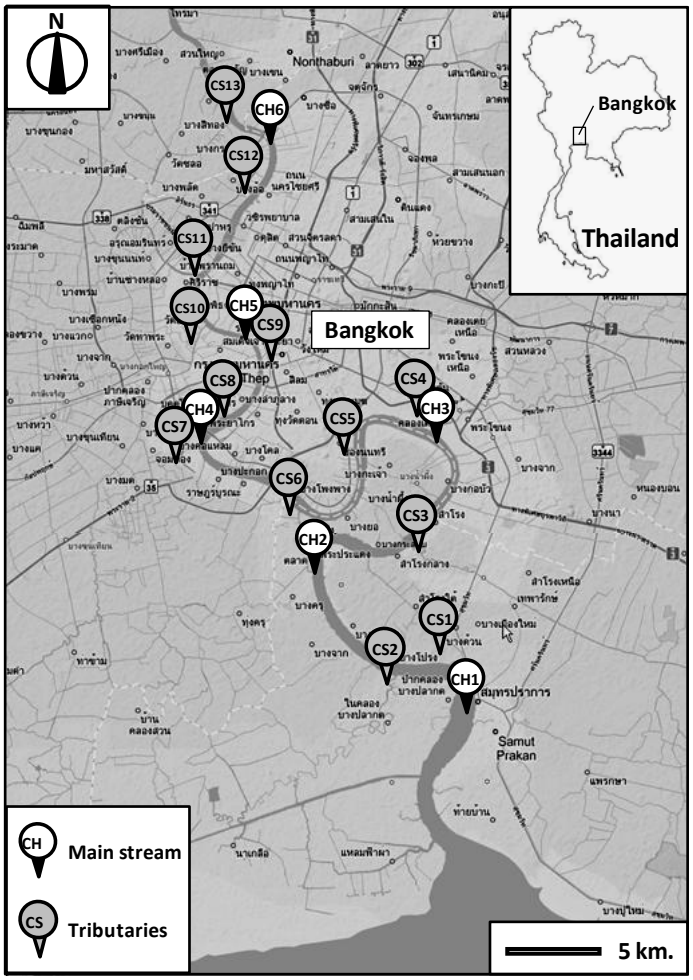
Central and Eastern Thailand was selected as the target area, where many big cities are located. The area is the biggest industrialized center of the country housing several industrialized zones. PFCs manufacturers as well as industries that use PFCs as their raw materials are located in this area. There is high possibility to detect these compounds in surface water. Field surveys were conducted in three major rivers (Chao Phraya River, Bangpakong River, and Tachin River), small rivers, reservoirs, and coastal areas. The sampling details are shown in Table 3.1.

Table 3.1 Details of sampling

Date	Place	Details	Sampling Point	Number of Samples
2007/9/19	Chao Phraya River (1st)	main stream (6), tributaries (13)	19	38
2008/6/24	Chao Phraya River (2nd)	main stream (6), tributaries (13)	19	38
2008/8/4	Chao Phraya River (3rd)	main stream (6), tributaries (13)	19	38
2007/12/7	Bangpakong River	main stream (12)	12	24
2008/10/23	Tachin River	main stream (6)	6	12
2008/7/2	Eastern Thailand Surface	river (5), resurvoir (3), coastal (4)	12	24
		Total	87	174

Chao Phraya River basin is the largest river system in Thailand, which supplies to a major metropolitan region. It covers 160,000 km^2, representing 30 percent of the country's total area and it is the source water for 23 million people (ONWRC, 2003). This study focused in the lower reach of Chao Phraya River, which flows through Bangkok city. There are dense residential, commercial and industrial areas along the

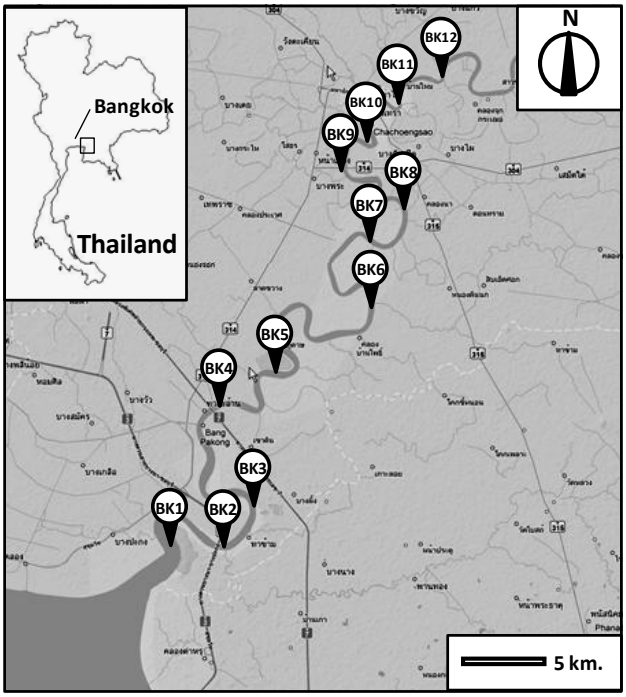
river. Figure 3.1 shows sampling points in Chao Phraya River. The sampling in Chao Phraya River was conducted on 2007/9/19, 2008/6/24, and 2008/8/4. Six sampling points in Chao Phraya River mainstream (CH1-CH6) and 13 points from the tributaries (CS1- CS13) were selected.



Source: Google Maps

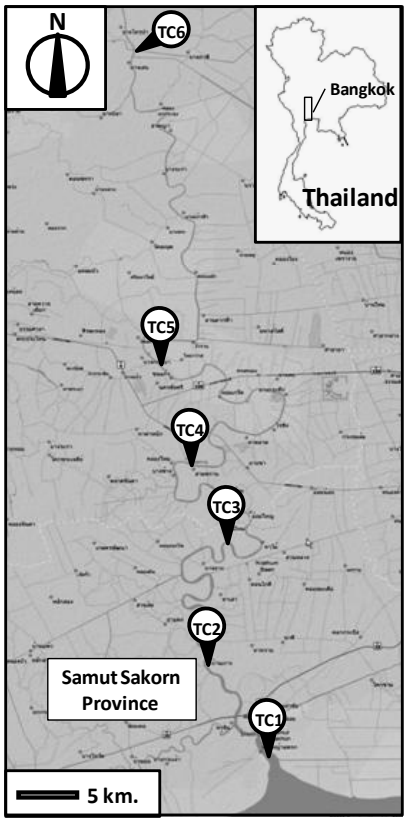
Figure 3.1 Sampling sites in Chao Phraya River

Bangpakong River was selected as the second river in the area. Bangpakong River basin is the most important watershed in Eastern Thailand. This river is a crucial source of water for irrigation, as well as for heavy and small industries, aquaculture, farming, and source for tap water in the area. The river basin covers 18,500 km^2. The sampling was conducted in Bangpakong River on 2007/12/7, where 12 samples (BK1-BK12) were collected from the mainstream. Figure 3.2 shows the sampling points in Bangpakong River.



Source: Google Maps

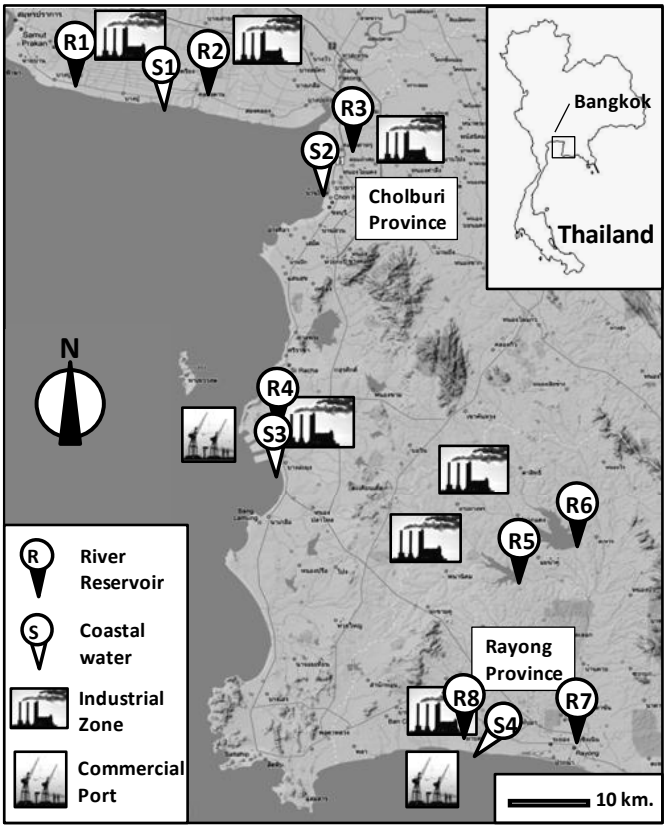
Figure 3.2 Sampling sites in Bangpakong River



Source: Google Maps

Figure 3.3 Sampling sites in Tachin River

Tachin River, which originates from Chao Phraya River, was also selected as the target area. Tachin River is located 10 km. away from western Bangkok. The river basin covers 13,681 km^2. Most of the areas (>90%) in the river basin are for irrigation activities. Six mainstream samples (TC1-TC6) were collected in mainstream of the river. The sampling was conducted on 2008/10/23. The sampling sites were shown in Figure 3.3.



Source: Google Maps

Figure 3.4 Sampling sites in small rivers, reservoirs, and coastal water

The last sampling was conducted in Eastern Thailand on 2008/7/2. Small rivers, reservoirs, and coastal water samples were also collected in addition to the major river systems. There are many large-scale industrial zones and ports in the area that might be the possible source of PFCs contamination to the surface water. Small rivers and reservoirs (R1-R8), located in the downstream of industrial zone discharges were selected. Coastal water samples were collected close to the ports and industrial zones discharges (S1-S4). Figure 3.4 shows sampling sites.

3.4 Materials and Method

3.4.1 Sample Collection

All samples were collected by grab-sampling using a plastic container. New 1.5 L narrow-neck PET bottles with screw caps were used as sample containers. Glass bottles and glassware apparatuses were avoided during the experiment as target compounds could attach to the glass (Hansen *et al*., 2002). Teflon materials were also avoided in the experiment because interferences may be introduced from them.

3.4.2 Sample Preparation

Liquid phase samples: A collected sample was filtered by 1 µm GF/B glass fiber filter to separate suspended solids. The suspended solid in filter was saved for further analysis by using Accelerated Solvent Extraction (ASE-200) from Dionex, Japan. Solid Phase Extraction (SPE) process was used for concentrating PFCs in liquid sample (Saito *et al*., 2003; Lien, 2007). The filtrate (1000 mL) was passed through a PresepC-Agri (C18) cartridge (Wako, Japan) that was preconditioned with 10 mL of LC/MS-grade methanol followed by 20 mL *Milli-Q* water manually. A flow rate of 10 mL/min was maintained through the cartridge. The above procedures were completed in Thailand and the cartridges were brought back to Japan for further analysis. In Japan, each cartridge was dried completely under vacuum. Then, the target compounds were eluted with 2×2 mL LC/MS-grade methanol into a polypropylene tube, evaporated to dryness with nitrogen gas, and reconstituted into LC/MS mobile phase (40% LC/MS-grade acetronitrile) to a final volume 2 mL. PFCs in filtrates were concentrated by a factor of 500 times. PFCs standards were spiked (10 ng/L) into a duplicated sample before LC/MS analysis to find their recoveries.

Solid phase samples: The suspended solids were separated by GF/B filter (Filtered volume: 1000 mL). The filters were air dried and inserted to ASE cells (Volume: 33 mL) for extraction. The extraction was done by using methanol as a solvent. The extraction process ran three cycles (15 min per one cycle) by using pressure 2000 psi

and temperature of 100ºC. Final extracted volume was 60 – 80 mL. Then, the extracted sample was diluted with LC/MS-grade *ultrapure* water into 1 L, loaded to a PresepC-Agri (C18) cartridge, and continued with the same procedure as liquid phase samples.

3.4.3 Instrumental Analysis and Quantification

Separations of PFCs were performed by using Agilent 1200SL high-performance liquid chromatography (HPLC), (Agilent, Japan). 10µL of extract was injected to a 2.1×100 mm (5 µm) Agilent Eclipse XDB-C_{18} column. Mobile phase consisted of (A) 5mM ammonium acetate in *ultrapure* water (LC/MS grade) and (B) 100% Acetronitrile (LC/MS grade). At a flow rate of 0.25 mL/min, the separation process started with initial condition of 30% (B), increased to 50% (B) at 16.5 min, then to 70% (B) at 16.6, held at 70% (B) for 3.4 min, went up to 90% (B) at 21 min, kept at 90% (B) for 1 min, and then ramped down to 30% (B). The total running time was 34 min for each sample. For quantitative determination, the HPLC was interfaced with an Agilent 6400 Triple Quadrupole (Agilent, Japan) mass spectrometer (MS/MS). Mass spectrometer was operated with the electro spray ionization (ESI) negative mode. Analyte ions were monitored by using multiple reactions monitoring (MRM) mode. The analytical parameters of each PFC are shown in Table 3.2.

Table 3.2 Analytical parameters of each PFC by HPLC/MS/MS analysis

Compound	No. of Carbon	Parent ion (*m/z*)	Daughter ion (*m/z*)	CE* (eV)	Retention time (min.)	LOQ (ng/L)
PFPA	C5-A	263	219	-15	2.1	0.5
PFHxA	C6-A	313	269	-15	3.2	0.4
PFHpA	C7-A	363	319	-15	5.4	0.3
PFOA	C8-A	413	369	-15	8.1	0.5
PFNA	C9-A	463	419	-15	10.9	0.4
PFDA	C10-A	513	469	-15	13.8	0.2
PFUnA	C11-A	563	519	-15	16.7	0.3
PFDoA	C12-A	613	569	-17	19.1	0.2
PFHxS	C6-S	399	80	-90	8.9	0.4
PFOS	C8-S	499	80	-90	15	0.2

Note: *CE = Collision Energy
S = Perfluorinated sulfonates (PFCSs)
A = Perfluorinated carboxylic acids (PFCAs)

3.4.4 Calibration and Validation

The calibration curves for quantification, consisting of six points covering 0.1–25 µg/L, generally provided linearity with determination coefficients (R^2) more than 0.999. Limit of detection (*LOD*) for LC/MS/MS was defined as concentration with signal to noise ratio (*S/N*) equal to 3:1. Practically, Limit of Quantification *(LOQ)* was used for quantifying analytes, which was defined by *S/N* 10:1 (Saito *et al.*, 2003; Hansen *et al.*, 2001). The identified *LOQ* was shown in Table 3.1. PFCs standards were spiked into the duplicated samples before LC/MS/MS analysis to find the MS detection efficiency. The duplicated analysis was also performed on all samples and coefficients of variations (*CV*) of concentrations were below 20%.

3.4.5 Analysis Recovery

The recovery rates were calculated by spiking PFCs standards into duplicated samples. PFCs standards were spiked before HPLC/MS/MS analysis for identifying the ionization suppression (or enhancement).

Table 3.3 Analysis recovery of surface water samples

Phase		Analysis Recovery									
		PFPA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFDoA	PFHxS	PFOS
Aqueous	Ave	0.49	0.64	0.85	0.98	1.06	1.05	1.09	0.99	1.01	1.14
	min	0.19	0.36	0.63	0.76	0.85	0.80	0.92	0.70	0.72	0.79
	max	0.79	1.02	1.05	1.36	1.34	1.37	1.39	1.35	1.35	1.47
Particulate	Ave	1.02	1.00	1.01	0.97	1.01	1.00	1.04	1.01	0.92	1.03
	min	0.89	0.87	0.82	0.70	0.84	0.90	0.93	0.73	0.64	0.86
	max	1.43	1.21	1.22	1.20	1.13	1.12	1.21	1.23	1.19	1.39

Note: Ave = Average, min = minimum, max = maximum

Table 3.3 shows the results of recovery rates of surface water samples. Recovery rates of aqueous phase samples were ranged from 49% to 114%; those of PFPA, PFHxA, and PFHpA were relatively low, 49 - 85%, when comparing with other PFCs (98 - 114%). These results indicated that there were interferences to PFPA, PFHxA, and PFHpA in LC-MS/MS analysis, especially in SPE. The recovery rate of PFOS and PFOA were

ranged from 76% to 136% and 79% to 147%, respectively. For the particulate phase samples, recovery rates were relatively high, ranged from 94% to 104%, indicating that there was less in ionization suppression or enhancement in the extracted samples.

3.5 Occurrences of PFCs in Major Rivers

3.5.1 PFCs in Solid and Liquid Phase

PFCs analysis was done in both dissolved and suspended solids (SS) samples. Figure 3.5 shows the relationship of PFOS and PFOA concentrations in liquid and solid phases. The concentrations of both PFOS and PFOA varied between rivers. Most of the plots of Chao Phraya River samples were near the linear line 1:1 representing that PFCs concentrations in the liquid and solid phase were equally found. In contrast, the results from Bangpakong and Tachin rivers were different. PFOS concentrations in Bangpakong River were found in dissolved samples with much higher value than in SS samples.

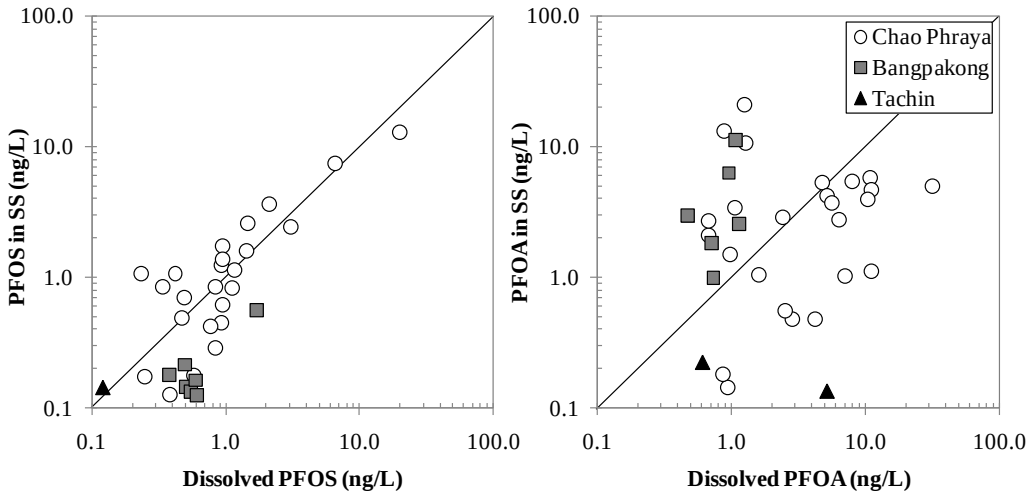


Figure 3.5 Relationship of PFOS and PFOA concentrations in liquid and solid phases in three major rivers

PFOA concentrations in Bangpakong River were found to be much higher value in solid phase, while those found in Tachin River were much higher in the liquid phase. It can be concluded that each river had a specific ratio of PFCs. The reason might be the

characteristics of wastewater that discharged to the river, river geographic or the location of the sources of PFCs. The result indicated that PFCs in the solid phase were also important for PFCs monitoring in the environment. To compare the result, the combined PFCs concentrations in liquid and solid phase were used in this study.

3.5.2 PFCs Concentrations

The river surveys were conducted in the lower reach of Chao Phraya River (urban area), Bangpakong River (sub-urban area), and Tachin River (sub-urban area). In this study, not only PFOS and PFOA but also other eight PFCs were measured in order to find their distribution. Table 3.4 summarized PFCs concentration in Chao Phraya River, Bangpakong River, and Tachin River. PFCs were detected in all samples indicating that most of the rivers in the area were contaminated by PFCs.

Table 3.4 PFCs concentration in Chao Phraya, Bangpakong and Tachin River

River	*n*		PFCs Concentration (ng/L)									
			PFPA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFDoA	PFHxS	PFOS
Chao Phraya	57	Ave	2.90	1.04	0.69	6.10	0.85	0.23	0.26	0.14	0.56	2.33
		SD	4.22	1.18	0.90	7.11	0.82	0.32	0.28	0.26	0.95	4.83
		Range	<LOQ-26.36	<LOQ-5.06	ND-4.56	1.05-36.75	ND-2.66	ND-1.31	ND-0.92	ND-1.04	ND-4.85	ND-33.06
Bangpakong	12	Ave	5.41	3.19	1.99	5.39	0.83	0.55	<LOQ	0.32	ND	0.61
		SD	4.33	1.63	1.37	3.42	0.46	0.24	-	0.16	-	0.58
		Range	ND-12.84	0.4-5.72	0.39-4.59	1.73-12.43	<LOQ-2.09	0.20-0.94	<LOQ	<LOQ-0.65	<LOQ	<LOQ-2.28
Tachin	6	Ave	2.32	0.23	0.43	1.01	0.52	0.51	0.29	0.92	0.54	0.64
		SD	1.21	0.22	0.46	1.93	0.96	0.97	0.77	1.10	1.41	1.24
		Range	ND-3.60	<LOQ-0.64	<LOQ-1.45	<LOQ-5.35	ND-2.70	ND-2.71	ND-2.04	<LOQ-3.24	ND-3.74	ND-3.41

Note: *n* = Number of samples, Ave = Average, SD = Standard diviation, ND = Not detected, LOQ = Limit of Quantification

The lower reach of Chao Phraya River passes through Bangkok city. Many domestic and industrial wastewater treatment plants discharge their effluent into this river. The samplings were conducted three times in Chao Phraya River. A total of 33 samples were collected. The average concentrations of each PFC were ranged from 0.14 to 6.10 ng/L. The average combined for the ten PFCs were 15.10 ng/L. PFOA, PFPA, and PFOS were the dominant PFCs with 41% (6.10 ng/L), 19% (2.90 ng/L), and 16% (2.33 ng/L), respectively (Figure 3.6). The range of PFOA, PFPA, and PFOS were between 1.05-

36.75 ng/L, <*LOQ*-26.36 ng/L, and *ND*-33.06 ng/L, respectively. The highest concentration was repeatedly detected in the same sampling site (CS3) with the combined ten PFCs concentration of 69.5 ng/L. The concentration level was higher than other tributaries that received wastewater from domestic activities, which was similar to previous studies (Prevedouros *et al.*, 2006; Lien *et al.*, 2008). CS3 receives the wastewater from many industrial activities in the catchment area. There are two large industrial zones in the catchment of CS3, which could be the possible source of PFCs contamination.

In Bangpakong River, 12 samples were collected from the mainstream. The average concentration of each PFC was ranged from *ND* to 5.41 ng/L. PFUnA and PFHxS were not detected in all samples. The dominant compounds were PFPA (29%), PFOA (28%), PFHxA (17%), and PFHpA (11%) (Figure 3.6). The average combined PFCs were 18.29 ng/L. The range of PFPA and PFOA were *ND* – 12.84 ng/L and 1.73 – 12.43 ng/L, respectively. The highest PFPA was detected in BK2, while the highest PFOA was detected in BK3. The results indicated that there must be the some sources releasing these compounds along the lower reach of Bangpakong River.

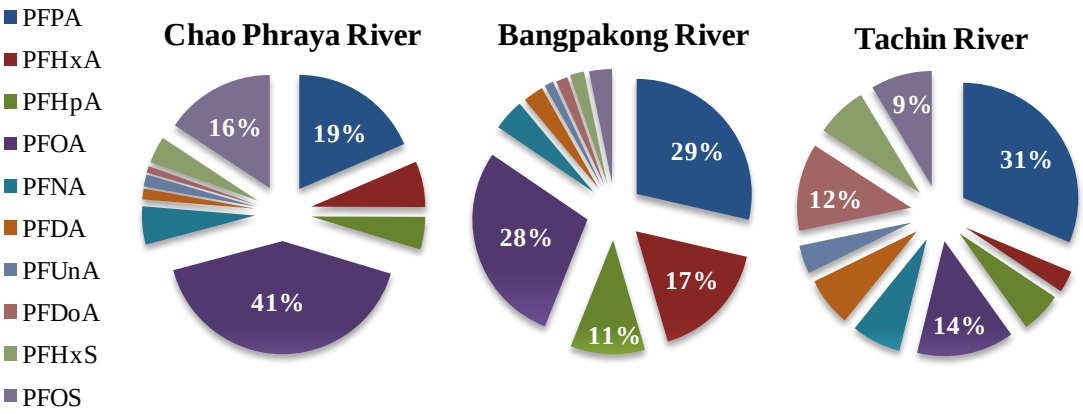


Figure 3.6 Relative abundance of PFCs in major rivers

The last sampling was conducted in Tachin River. Six samples in the mainstream were collected to identify PFCs concentrations. Compared to Chao Phraya and Bangpakong River the concentration in Tachin River was quite lower. The average concentrations of

each PFC varied from 0.29 to 2.32 ng/L. The average combined concentration of ten PFCs was 7.40 ng/L. PFPA, PFOA, PFDoA, and PFOS were the dominant PFCs with 31%, 14%, 12%, and 9%, respectively.

From Figure 3.6, the different percentage patterns among three major rivers were observed. The relative abundance of PFCs in each river was unique. This can be a useful parameter to identify the source of PFCs contaminations. For example, the relative abundance of PFCs in Chao Phraya River was comparable to the influent of Water Treatment Plant for Bangkok city in Section 6.4.2.

3.5.3 PFOS and PFOA Contaminations

From three Chao Phraya River surveys, PFOS and PFOA were detected with the concentrations above *LOQ* in all samples. The concentrations in the mainstream varied in the range of 2.79 – 3.41 ng/L PFOS and 5.90 – 12.37 ng/L PFOA with the average 1.81 ng/L for PFOS and 8.66 ng/L for PFOA.

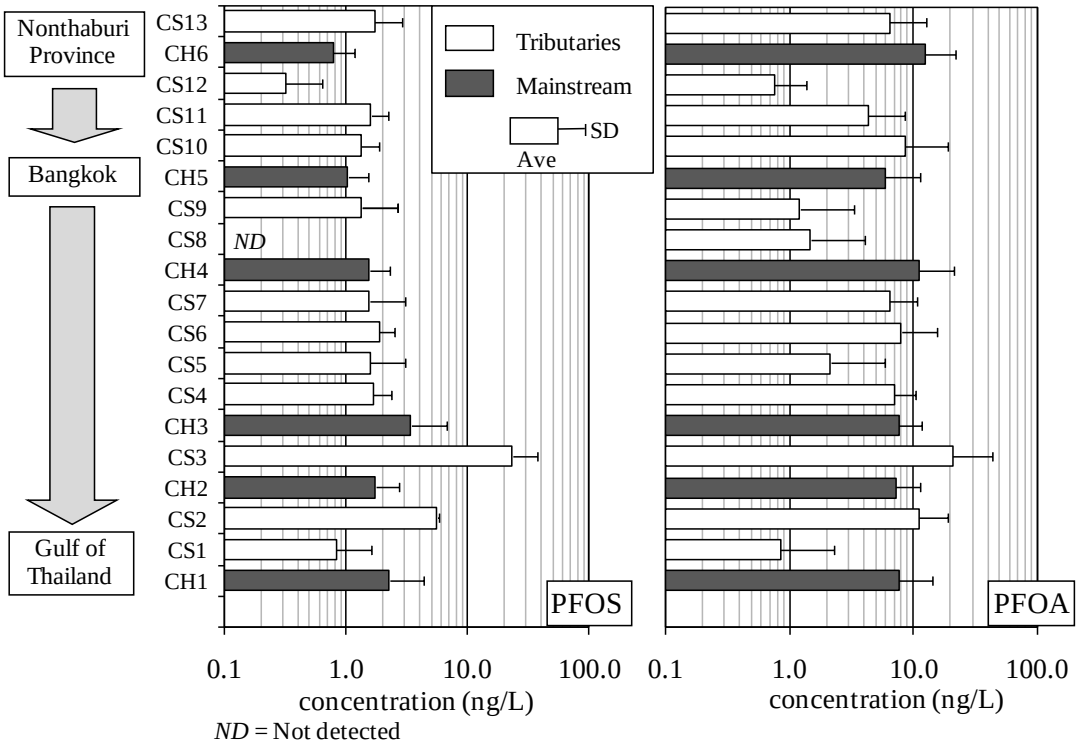


Figure 3.7 PFOS and PFOA concentration in Chao Phraya River

Figure 3.7 shows PFOS and PFOA contamination profiles in Chao Phraya River mainstream and tributaries. PFOS concentrations were gradually increasing from upstream site CH6 (Nonthaburi Province) to most downstream site CH1 (Gulf of Thailand, river outlet), while PFOA concentration were quite similar along the river. PFOS increased from 0.79 to 2.29 ng/L, showing that there must be many contamination sources along the river including point sources and non-point sources. The elevated PFOS and PFOA were detected in tributary CS3 with concentration of 23.58 ng/L and 20.74 ng/L, respectively. CS3 receives the wastewater from many industrial activities in the catchment area as described in the previous section.

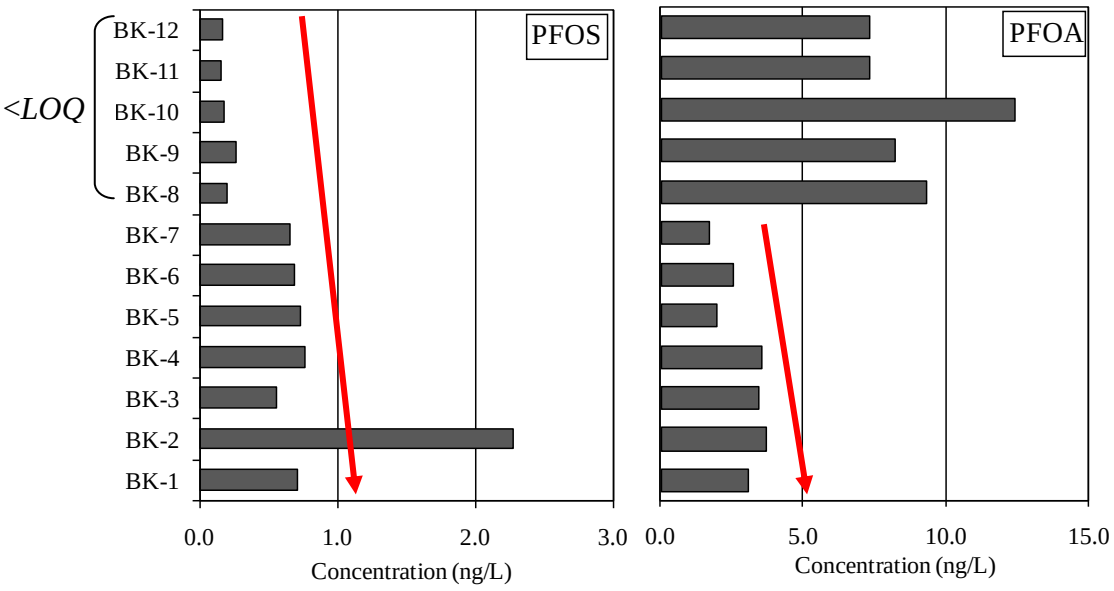


Figure 3.8 PFOS and PFOA concentration in Bangpakong River

Figure 3.8 shows Bangpakong River survey (sub-urban area), where 12 mainstream samples were collected. PFOS and PFOA were detected in all samples. The concentration of PFOS and PFOA were lower compared to Chao Phraya River. PFOS and PFOA concentrations were ranged from <*LOQ* – 2.3 ng/L and 1.73 – 12.43 ng/L, respectively. The average PFOS concentration was recorded at 0.61 ng/L, while PFOA was 5.39 ng/L. PFOA was highly detected in this area between BK8 and BK12 with the average concentration at 8.92 ng/L, while average PFOA concentration was only 2.86 ng/L from BK7 to BK1. A city was located at one side of the river in the area between

BK8 to BK12. It is evident there were some sources of PFOA in that city area. In contrast, PFOS was relatively lower (<*LOQ*) in the upper reach of the river (BK12-BK8). From BK7, PFOS was gradually increasing. The elevated PFOS was detected at BK2, where some industries and a power plant were located.

In Tachin River, where most of the catchment areas are covered with agriculture, the concentrations range of PFOS and PFOA were relatively low of *ND* – 3.41 ng/L and <*LOQ* – 5.35 ng/L, respectively. The average concentrations were at 0.64 ng/L for PFOS and 1.01 ng/L for PFOA. There were very low contamination of PFOS and PFOA in the upper reach of the river (TC3 – TC6). In the lower reach, the river passes through a city. At this point, the elevated PFOS was detected at TC2 (3.41 ng/L), while the highest PFOA was detected near the river outlet site TC1 (5.35 ng/L).

Table 3.5 Loading of PFOS and PFOA from major rivers

River	Sampling date	Flow rate ($x10^6$ m^3/d)	Loading (g/d)	
			PFOS	PFOA
Chao Phraya	2007/9/19	70.2	199.9	322.8
	2008/6/24	30.2	27.4	456.1
	2008/8/4	24.3	97.9	81.7
		Average	*108.4*	*286.9*
Bangpakong	2007/12/7	10.8	7.7	23.7
Tachin	2008/10/23	3.3	2.4	13.0
		Total	*118.6*	*323.6*

Furthermore, to calculate PFCs mass loading from each river, flow rate data were obtained from Royal Irrigation Department, Thailand (RID, 2008). Flow rates (monthly average) of Chao Phraya River were reported to be at 30.2 x 10^6 m^3/d in June, 24.3 x 10^6 m^3/d in August, and 70.23 x 10^6 m^3/d in September. Flow rate of Bangpakong River was at 10.8 x 10^6 m^3/d in December and average flow of Tachin River was at 3.3 x 10^6 m^3/d in October. Table 3.4 summarizes the loading rates of PFOS and PFOA from three major rivers. The average loading rates of PFOS and PFOA from Chao Phraya River were 108.4 g/d and 286.9 g/d, respectively. Loading rates from Chao Phraya River were accounted for 91% PFOS and 88% PFOA of total three river discharges. Other two

rivers, which have lower flow rate, released lesser PFCs. Bangpakong River discharged PFOS valued at 7.7 g/d and PFOA 23.7 g/d, while Tachin River discharged PFOS of 2.4 g/d and PFOA about 13.0 g/d. The total of 118.6 g/d PFOS and 323.6 g/d PFOA were released daily from the three rivers to the Gulf of Thailand, where the important activities were food sources for domestic and exports. It is possible that this amount of PFCs entered the food chain and caused some effects to the environment and human.

3.5.4 Repeated Sampling in Chao Phraya River

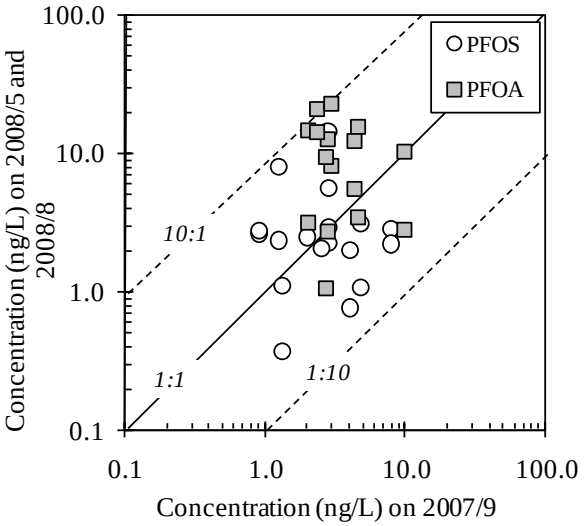


Figure 3.9 Relationship of PFOS and PFOA concentration in 2007 and 2008

Repeated sampling in Chao Phraya River was conducted. Figure 3.9 shows the relationship between the surveys in 2007 and 2008 on PFOS and PFOA concentrations in Chao Phraya River for the same sampling point. The plots varied around the linear line 1:1 showing that PFCs were continuously discharged to the environment at the comparable level. However, 62% of PFOS plots were below 1:1 line, indicating that the PFOS concentration was declining in 2008 as compared to 2007. The recent studies have also shown declining concentration of PFOS in environmental, and blood samples following the phase-out of PFOS production of 3M company in 2000 (Tagaki *et al.*, 2008; Renner, 2008). In contrast, 68% of PFOA plots were above the linear 1:1 line, showing that PFOA concentration was increasing in 2008. Moreover, there are 25% of PFOA plots that exceed the 90% increase. The result shows the rising of PFOA usage.

Although USEPA released the PFOA stewardship program in 2006 to reduce the PFOA production (USEPA, 2006b), PFOA were still detected and even increased in surface waters. The countermeasure of PFOA problems should be implemented in the near future.

3.6 Occurrences of PFCs in Small Rivers, Reservoirs, and Coastal Water

3.6.1 PFCs Concentrations

The survey was conducted in small rivers, reservoirs, and coastal water around Eastern Thailand. Sampling points were selected near the potential sources of PFCs contamination from the industrial zones. PFCs concentrations in surface water around Eastern Thailand are as summarized in Table 3.6. PFCs were detected in all samples, indicating that most of the surface waters in this area were contaminated by PFCs.

Table 3.6 PFCs concentration in small rivers, reservoirs, and coastal water

Sample	*n*		PFCs Concentration (ng/L)									
			PFPA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFDoA	PFHxS	PFOS
Small River	5	GM	16.9	12.1	9.6	107.7	4.7	3.1	2.3	2.3	31.3	15.4
		Range	4.1-26.0	3.3-23.1	3.9-15.7	14.8-402.3	2.8-6.6	2.0-4.2	1.8-206	1.6-2.6	0.6-122.7	3.1-36.9
Reservoir	3	GM	5.3	5.6	8.4	35.4	174.6	3.0	14.5	2.2	3.6	212.2
		Range	2.4-8.0	4.1-7.5	5.6-13.5	16.7-72.4	3.2-516.8	2.4-4.0	2.4-38.5	2.0-2.5	2.0-5.0	5.3-572.5
Coastal water	4	GM	7.9	4.4	5.6	41.1	3.8	1.6	2.6	0.8	5.0	8.6
		Range	1.5-12.3	2.7-6.4	3.8-7.2	10.9-101.5	2.2-5.9	0.7-2.8	1.4-4.1	0.6-1.0	1.0-14.9	4.0-16.4

Note: *n* = Number of samples, GM = Geometric Mean

The geometric mean (GM) concentrations of each PFC were ranged from 2.3 to 107.7 ng/L in small rivers, 2.2 to 212.2 ng/L in reservoirs, and 0.8 to 41.1 in coastal water samples. In small rivers (R1, R2, R4, R7, and R8), the geometric mean combined ten PFCs was at 205.4 ng/L. PFOA, PFHxS, PFPA and PFOS were the dominant PFCs with 52% (107.7 ng/L), 15% (31.3 ng/L), 8% (16.9 ng/L), and 8% (15.4 ng/L), respectively (Figure 3.10). The highest concentration was detected in the sampling site R4 with the combined ten PFCs concentration at 503.9 ng/L, much higher compared to Chao Phraya River (69.5 ng/L). This river receives wastewater from a large industrial zone and the biggest port in Eastern Thailand. These places might have been the sources of PFCs.

Further studies of PFCs contamination in the selected industrial zones are described in the next chapter.

Three reservoirs (R3, R5, and R6) near industrial zones were selected as the target area. The geometric mean combined PFCs was at 464.8 ng/L. PFOS, PFNA, and PFOA were the dominant compounds with 46% (212.2 ng/L), 37% (174.6 ng/L), and 8% (35.4 ng/L), respectively (Figure 3.10). The highest combined ten PFCs concentration was at 1234.6 ng/L at R3, where one industrial zone was located.

Coastal water samples (S1-S4), near the rivers outlet (Figure 3.4), were collected to evaluate PFCs concentrations around the Gulf of Thailand. The geometric mean combined ten PFCs was at 81.4 ng/L. The dominant PFCs were PFOA (51%), PFOS (10%), PFPA (10%), and PFHpA (7%). The highest combined PFCs was detected in S3 (130.3 ng/L), where located near the outlet of the highest concentration in river (R4).

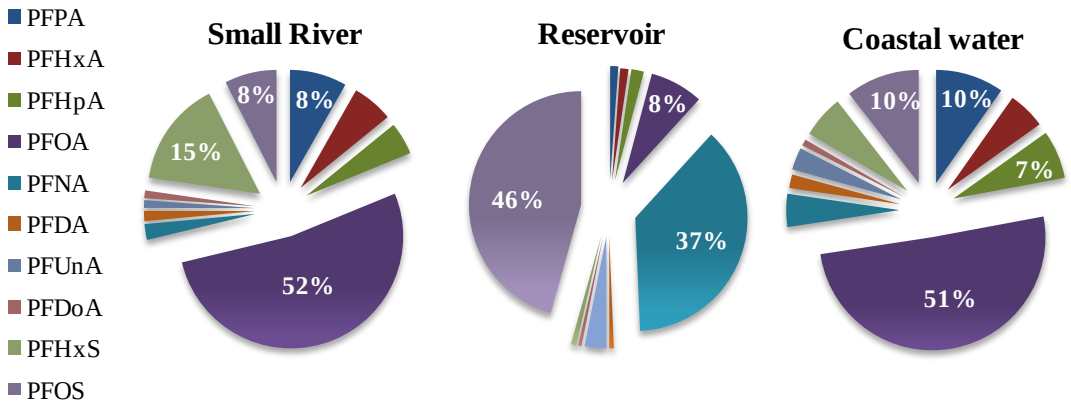
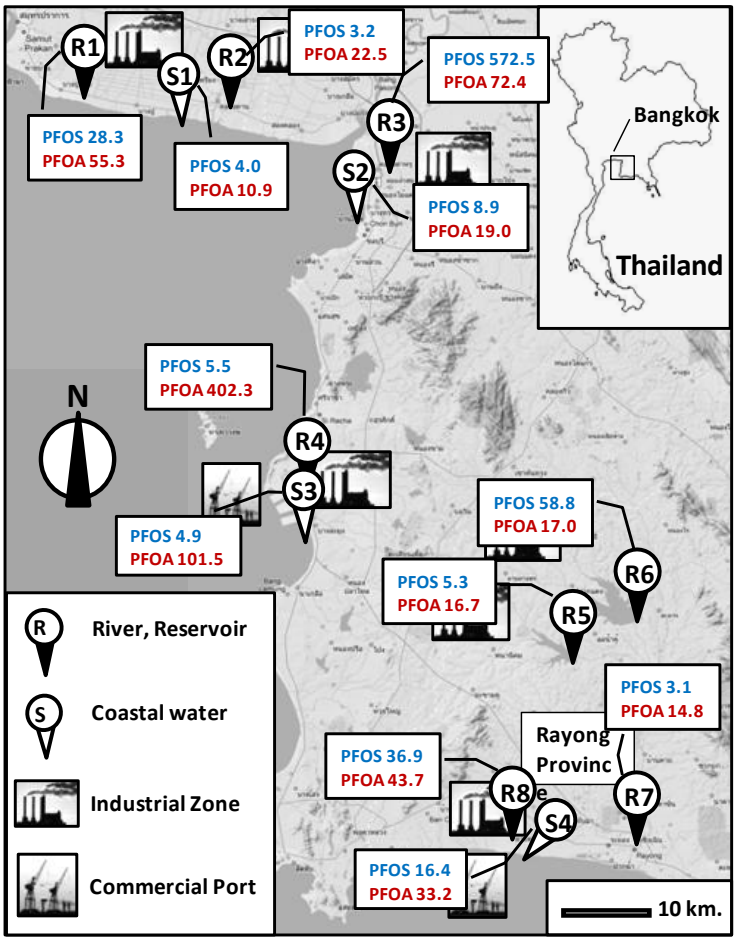


Figure 3.10 Relative abundance of PFCs in small rivers, reservoirs, and coastal water

3.6.2 PFOS and PFOA Contaminations

PFOS and PFOA concentrations in small rivers and reservoirs were much higher than detected in major rivers. The higher concentrations are probably from the less dilution factor and higher discharges of these compounds. The range of PFOS and PFOA concentration in small rivers were at 3.1 – 36.9 ng/L and 14.8 – 402.3 ng/L respectively.

The concentrations ranges in reservoirs were at 5.3–572.5 ng/L for PFOS and 16.7–72.4 ng/L for PFOA. The highest PFOS in a river was detected at R8 (36.9 ng/L), where wastewater effluents were discharged from an industrial zone, while the highest PFOA was found in R4 with the concentration 402.3 ng/L. In reservoirs, the highest PFOS and PFOA were detected at the same sampling site R3. The contamination levels were comparable to the higher range of PFOS and PFOA detected in Japan (Saito *et al.*, 2004). The highest PFOS and PFOA in coastal water were found in S4 (16.4 ng/L) and S3 (101.5 ng/L), respectively. The PFOS range was comparable to those found in Tokyo and Osaka bay (Taniyasu *et al.*, 2003). The result indicated that PFOS and PFOA contamination levels in Thailand's industrial area were also comparable to those in the water environment of Japan.



Source: Google Maps

Figure 3.11 PFOS and PFOA concentration in small rivers, reservoirs, and coastal water samples

Figure 3.11 shows PFOS and PFOA concentrations in small rivers, reservoirs, and coastal water samples. The figure shows the relationship between PFOS and PFOA in the rivers, reservoirs and coastal water. Rivers and reservoirs finally release PFCs to the coastal areas, where PFCs could be highly detected. S1 locates near the outlet of R2. PFOS and PFOA concentration in the coastal water were less than in the river due to the dispersion of PFCs in the sea. As Reservoir R3 was located inside an industrial zone and it was not connected to the river, the concentrations at the reservoir were much higher than nearby coastal water. R4 receives wastewater from the industrial zones and one of the largest ports in Thailand.

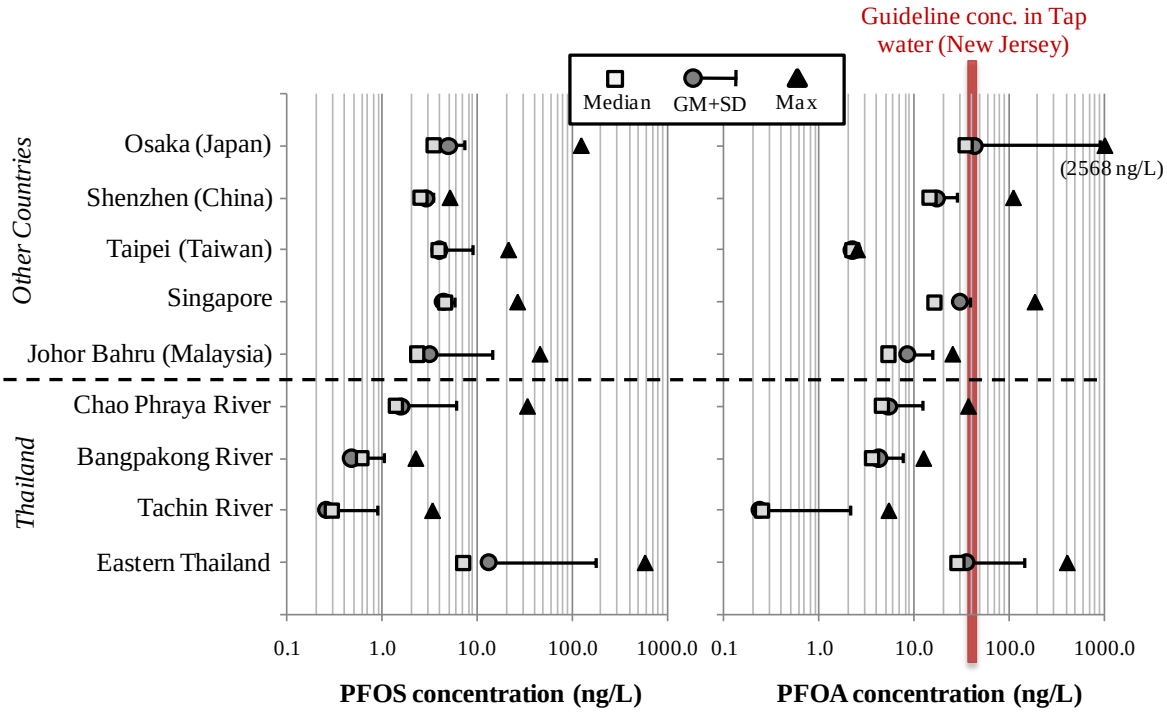
Overall, the rivers and reservoirs, which are located in the downstream of the industrial zones, showed high PFCs contaminations. The PFCs in rivers and reservoirs were discharged to the Gulf of Thailand. This amount of PFCs could contaminate the fish and aquaculture in the area, where both are important food sources for Thai people and for export purposes. The further study should concern about the fate and transportation of these compounds to the food chain and pathway to the human cycle.

3.7 Comparing PFCs Concentration in Surface Water among Other Asian Cities

Figure 3.12 shows concentration of PFOS and PFOA concentrations in surface water samples in Thailand comparing with other Asian cities (Osaka, Shenzhen, Taipei, Singapore, and Johor Bahru) (Lien *et al*., 2008; Tanaka *et al.*, 2008; Kunacheva *et al*., 2009). Bangpakong and Tachin River are located in sub-urban area, where there are less industrial activities. PFOS concentrations in Bangpakong and Tachin River were very low compared to other countries. However, PFOS levels in Chao Phraya River and surface water in Eastern Thailand were comparable to those in other Asian countries. Eastern Thailand surface water, where the sampling points located near the industrial zones, contained the highest concentration levels. The reason could be from higher discharges of PFCs and low dilution factors comparing to major rivers. The further study on PFCs loading should be conducted in these areas to evaluate better understanding in PFCs contamination.

Comparing to PFOS, PFOA concentration was found higher in the samples. While the lowest PFOA level was detected in Tachin River, the concentrations in Chao Phraya River and Bangpakong River were comparable to those in Taipei and Malaysia. However, PFOA concentrations of these two rivers were much less than those in Osaka, Shenzhen, and Singapore. PFOA level in surface water in Eastern Thailand was at the similar level detected in Osaka, where Saito *et al.* (2004) noted that the highest PFOA area was in Japan.

Although, less PFCs concentrations were detected in Thai rivers, this still does not verify that PFCs discharged in Thailand are lower than other countries. The flow rate has an effect in PFCs concentration level. The PFCs concentrations in Thai major rivers were less than rivers in other countries such as Yodo River in Japan. However, PFOS (108.4 g/d) and PFOA (558.1 g/d) loading in Chao Phraya River were much higher than in Yodo River (PFOS 40 g/d and PFOA 330 g/d, Lien *et al.*, 2008) due to the higher flow rate.



Note: GM = Geometric mean, SD = Standard deviation

Figure 3.12 Comparing PFOS and PFOA concentration in surface water with other countries

Moreover, New Jersey Department of Environmental Protection (2007) reported that the guideline value of PFOA in drinking water was at 40 ng/L. At this PFOA level, some samples in Osaka, Singapore, and Eastern Thailand were above the guideline. The surface waters in these areas are the sources of tap water. As conventional and advanced water treatment plants were also not effective to remove PFOA (Takagi *et al*., 2008), these compounds might cause an effect to the people living in the area.

3.8 Summary

PFCs were detected in all samples, indicating that most of the surface water in this area was contaminated by PFCs. The ratios of PFCs concentrations in liquid and solid phases were varied between samples. The samplings were conducted three times in Chao Phraya River. The average combined ten PFCs was at 15.10 ng/L. PFOA, PFPA, and PFOS were the dominant PFCs with 41% (6.10 ng/L), 19% (2.90 ng/L), and 16% (2.33 ng/L), respectively. PFOS and PFOA concentrations in the mainstream varied in the range of 2.79 – 3.41 ng/L and 5.90 – 12.37 ng/L, respectively, with the average of 1.81 ng/L for PFOS and 8.66 ng/L for PFOA. PFOS increased from 0.79 to 2.29 ng/L along the river, indicating that there should be many contamination sources including point sources and non-point sources.

In the Bangpakong River, the average combined PFCs were at 18.29 ng/L. The dominant compounds were PFPA (29%), PFOA (28%), PFHxA (17%), and PFHpA (11%). The concentration of PFOS and PFOA were lower compared to Chao Phraya River. PFOS and PFOA concentrations were ranged from <*LOQ* – 2.3 ng/L and 1.73 – 12.43 ng/L, respectively. Compare to Chao Phraya and Bangpakong River the concentration in Tachin River was quite lower. The average combined ten PFCs was at 7.40 ng/L. PFPA, PFOA, PFDoA, and PFOS were the dominant PFCs with 31%, 14%, 12%, and 9%, respectively. The concentrations of PFOS and PFOA were relatively low ranging from *ND* – 3.41 ng/L and <*LOQ* – 5.35 ng/L, respectively. The average concentrations were at 0.64 ng/L PFOS and 1.01 ng/L PFOA. From the three major rivers, the total of 118.6 g/d PFOS and 323.6 g/d PFOA were released daily from the

three rivers to the Gulf of Thailand. The elevated PFOS and PFOA were detected in sampling sites, which receives wastewater from many industrial activities.

Moreover, the survey was also conducted in small rivers, reservoirs, and coastal water around Eastern Thailand. Sampling points were selected as the potential of PFCs contamination sources from the industrial zones. Compared to major rivers, much higher PFCs concentration was detected in these samples. The geometric mean (GM) concentrations of each PFC were ranged from 2.3 to 107.7 ng/L in small rivers, 2.2 to 212.2 ng/L in reservoirs, and 0.8 to 41.1 in coastal water samples. PFOS and PFOA concentration in small rivers varied from 3.1 – 36.9 ng/L and 14.8 – 402.3 ng/L. The concentrations in reservoirs were ranged at 5.3 – 572.5 ng/L PFOS and 16.7 – 72.4 ng/L PFOA. Rivers and reservoirs discharged PFCs to the sea, where PFCs could be detected in the coastal water. PFOS and PFOA concentration in the coastal water were less than in the rivers due to the dispersion of PFCs in the sea. Comparing with other Asian cities, PFOS concentrations in Bangpakong and Tachin River were very low. However, PFOS levels in Chao Phraya River and surface water in Eastern Thailand were comparable to those in other Asian countries.

Overall, higher PFCs contaminations were detected in the industrial areas, where might be the source of these compounds. There was even PFCs contaminations detection in rivers and reservoirs, which were located in the downstream of the industrial zones. The PFCs in rivers and reservoirs were discharged to the Gulf of Thailand, where is the important food source for Thai people and for export purposes.

Chapter 4

Perfluorinated Compounds Contamination in Industrial Zones, Thailand

4.1 Introduction

Perfluorinated compounds (PFCs) have been manufactured for use in a large variety of industrial and commercial products for more than 50 years (Giesy and Kannan, 2002). PFCs are widely used in the manufacturing industry as surfactants, surface treatment, fire retardants, and coating materials. These compounds are fully fluorinated organic compounds with strong carbon – fluorine bonds that make PFCs strong and persistent in the environment. The dominant PFCs, Perfluorooctane sulfonate (PFOS) and Perfluorooctanoic acid (PFOA), recently became a new group of persistent organic compounds (POPs) that are persistent, bioaccumulated, and have potential to cause adverse effects on humans and the environment (USEPA, 2006a). Although PFCs related regulations have been used in many countries, these compounds still have been found in the environment and biota (EC, 2006; USEPA, 2006b; Berger *et al*., 2004; Saito *et al*., 2003; Sinclair *et al*., 2004). To date, the sources of contamination of these compounds have not been fully understood. However, some reports revealed that their major sources seemed to be related to industrial activities (Taniyasu *et al*., 2005; Hansen *et al*., 2002; Lien, 2007).

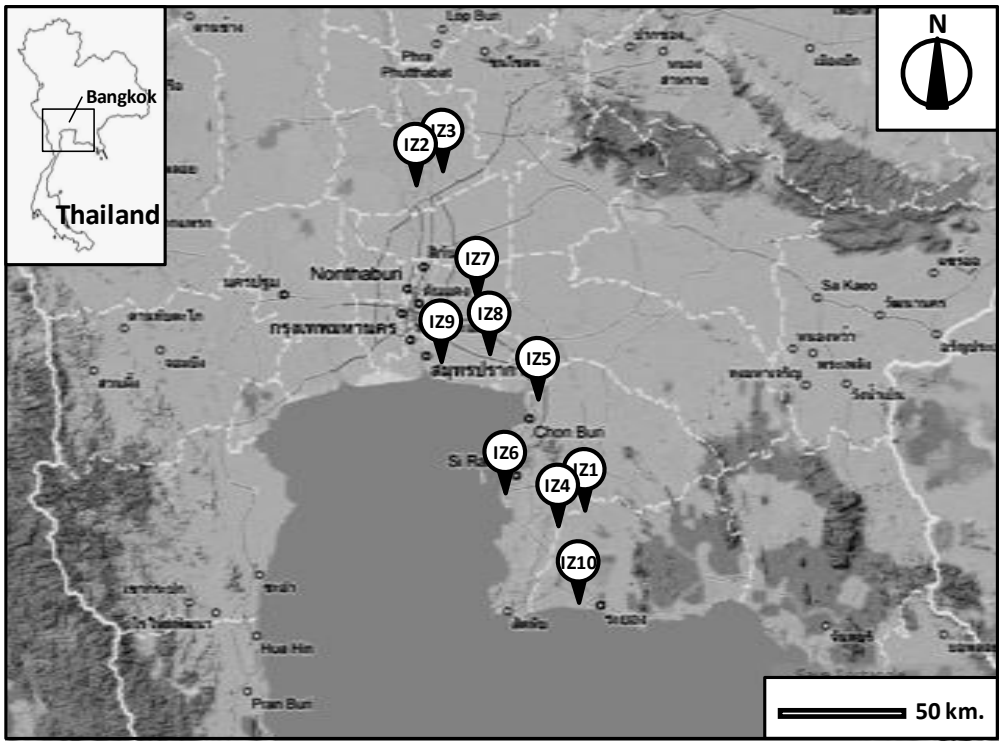
Recently, due to the PFCs regulation released in developed countries, the major PFCs manufacturers and PFCs using companies have shifted their factories to developing countries especially in the Southeast Asia where few researches have reported about PFCs contamination. In Chapter 3, the PFCs contaminations in Thai surface water were identified and discussed. Most of surface waters in the area were contaminated by PFCs. The elevated PFCs places were recognized. Based from the results from Chapter 3, ten industrial zones, where many industries were established, were selected for our study.

4.2 Objectives

The objectives of this chapter were (1) to examine the recovery of PFCs analysis method for different wastewater samples in Thai industrial zones (IZs), (2) to determine the concentration and loadings of PFCs released by IZs, and (3) to investigate the influence of PFCs contamination from IZs to nearby surface water.

4.3 Sampling Sites

Samplings were conducted in the selected ten industrial zones (IZ1-IZ10), which are the major industrial sectors in the area (Figure 4.1). There are more than 196 factories located in each industrial zone. Many types of industries were located in the area which included electronics, chemical, paper, plastic, glass, etc. that has potential of releasing PFCs. All industries discharge their wastewater into central wastewater treatment plant (WWTP) of each IZ.



Source: Google Maps

Figure 4.1 Location of selected industrial zones

Central WWTP has a set of water quality standards that each industry have to follow before sending it to WWTP such as BOD < 500 mg/L, COD < 750 mg/L, and other parameters. The important parameter is surfactants (< 30mg/L), which also include PFCs. However, 30 mg/L range is much higher than trace level of ng/L or mg/L. In their central WWTPs, conventional processes such as Activated Sludge (AS), Rotating Biological Contactor (RBC), Sequencing Batch Reactor (SBR), and wetland are commonly used except in IZ5, which uses SBR coupled with advanced processes. Table 4.1 shows sampling date and details of the selected industrial zones.

Table 4.1 Sampling date and information of the selected industrial zones

Industrial Zones	Sampling Date	No. of Industries	Conventional Process type	Advanced Process type	Flow rate (m^3/d)
IZ1	2007/12/6	478	AS, Wetland	None	30,000
IZ2	2008/2/8	316	AS	None	12,000
	2008/8/22				
IZ3	2008/8/22	270	AS	None	16,800
IZ4	2008/6/27	200	AS	None	14,000
IZ5	2008/6/28	484	SBR	Sand filtration,	20,000
	2008/8/29			MF, RO	
IZ6	2008/8/29	398	AS	None	23,700
IZ7	2007/7/25	550	AS	None	26,000
IZ8	2007/9/18	320	AS	None	21,000
IZ9	2007/8/24	1120	AS	None	28,900
IZ10	2008/10/30	196	AS	None	11,200

Note: AS = Activated Sludge, RBC = Rotating Biological Contactor,
SBR = Sequencing Batch Reactor, MF = Microfiltration membrane,
RO = Reverse osmosis membrane

Field surveys were conducted in ten industrial zones. Influent, aeration tank, and effluent samples were collected from central WWTP of each IZ. Effluent samples from selected industries inside industrial zones were also collected. Due to the limitation of permission in the sampling, effluent samples from industries were only collected from IZ2, IZ3, IZ4, and IZ8. Tap water samples, which were used in industrial production processes, were also collected to identify the background concentration of the industrial zones. The repeated samplings were conducted in some IZs (IZ2 and IZ5) to identify reproducibility of these compounds. Details of the sampling were shown in Table 4.2.

Table 4.2 Sampling details in IZ1 – IZ10

Date	Place	Details	Sampling Point	Number of Samples
2007/5/25	IZ7	WWTP (Tap, Inf, Eff)	3	6
2007/8/24	IZ8	WWTP (Tap, Inf, Ae, Eff) and Industry effluent (5)	8	16
	IZ9	WWTP (Tap (3), Inf (3), Eff (3))	9	18
2007/9/18	IZ8	WWTP (Tap, Inf, Ae, Sed, Eff) and Industry effluent (6)	11	22
2007/12/6	IZ1	WWTP (Tap (2), Inf (2), Eff(3), River (2), Reservoir (2)) and Industry effluent (8)	19	38
2008/2/8	IZ2	WWTP (Tap, Inf, Ae, Sed, Eff, Pond, Sludge) and Industry effluent (5)	12	24
	IZ3	WWTP (Tap, Inf, Ae, Eff, Pond) and Industry effluent (5)	10	20
2008/6/28	IZ4	WWTP (Tap, Inf, Ae, Eff) and Industry effluent (4)	8	16
	IZ5	WWTP (Tap, Inf, Ae, Eff, RO)	5	10
2008/8/22	IZ2	WWTP (Tap, Inf, Ae, Sed, Eff) and Industry effluent (5)	10	20
	IZ3	WWTP (Tap, Inf, Ae, Eff) and Industry effluent (3)	7	14
2008/8/29	IZ5	WWTP (Tap, Inf, Ae, Eff, before RO, RO, ROR)	7	14
	IZ6	WWTP (Tap, Inf, Ae, Eff)	4	8
2008/10/30	IZ10	WWTP (Tap, Inf, Ae, Eff, River)	5	10
		Total	118	236

4.4 Materials and Methods

4.4.1 Sample Collection

Samples were collected by grab-sampling using a polypropylene container. New 1.5 L narrow-neck PET bottles with screw caps were used as sampling containers. PET bottles were washed with methanol and dried prior to use. Containers were also rinsed three times with sample before collection.

4.4.2 Sample Preparation and Extraction

Liquid phase samples: A collected sample was filtered by 1 µm GF/B glass fiber filter to separate suspended solids. The filter was then further analyzed by using Accelerated Solvent Extraction (ASE-200). The filtrates 500 mL were then loaded to PresepC-Agri (C18) cartridge, which was used for concentrating PFCs (Saito *et al*., 2003; Lien, 2007).

The cartridge was preconditioned before use. The above procedures were completed in Thailand and the cartridges were brought back to Japan for further analysis. In Japan, each cartridge was dried, eluted with 2×2 mL LC/MS-grade methanol, evaporated to dryness with nitrogen gas, and reconstituted into LC/MS mobile phase (40% LC/MS-grade acetronitrile) to a final volume 2 mL. PFCs in filtrates were concentrated by a factor of 250 times. PFCs standards were spiked (10 ng/L) into a duplicated sample before LC-MS/MS analysis to find their recoveries.

Solid phase samples: The suspended solids phase was separated by GF/B filter (Filtered volume: 500 mL). The filters were air dried and inserted to ASE cells for extraction. The extraction was done by using Methanol as a solvent. Then, the extracted sample was diluted with LC/MS-grade *ultrapure* water into 1 L, loaded to a PresepC-Agri (C18) cartridge, and continued with the same procedure as liquid phase samples.

4.4.3 Instrumental Analysis and Quantification

Table 4.3 Analytical parameters of each PFC by HPLC/MS/MS analysis

Compound	No. of Carbon	Parent ion (*m/z*)	Daughter ion (*m/z*)	CE* (eV)	Retention time (min.)	LOQ (ng/L)
PFPA	C5-A	263	219	-15	2.1	0.5
PFHxA	C6-A	313	269	-15	3.2	0.4
PFHpA	C7-A	363	319	-15	5.4	0.3
PFOA	C8-A	413	369	-15	8.1	0.5
PFNA	C9-A	463	419	-15	10.9	0.4
PFDA	C10-A	513	469	-15	13.8	0.2
PFUnA	C11-A	563	519	-15	16.7	0.3
PFDoA	C12-A	613	569	-17	19.1	0.2
PFHxS	C6-S	399	80	-90	8.9	0.4
PFOS	C8-S	499	80	-90	15	0.2

Note: *CE = Collision Energy
S = Perfluorinated sulfonates (PFCSs)
A = Perfluorinated carboxylic acids (PFCAs)

Separation of PFCs was performed by using Agilent 1200SL high-performance liquid chromatography (HPLC). Extract 10µL was injected to a 2.1x100 mm (5 µm) Agilent

Eclipse XDB-C_{18} column. Mobile phase consisted of (A) 5mM ammonium acetate in *ultrapure* water (LC/MS grade) and (B) 100% Acetronitrile (LC/MS grade). At a flow rate of 0.25 mL/min, the separation process started with initial condition of 30% (B), increased to 50% (B) at 16.5 min, then to 70% (B) at 16.6, held at 70% (B) for 3.4 min, went up to 90% (B) at 21 min, kept at 90% (B) for 1 min, and then ramped down to 30% (B). The total running time was 34 min for each sample. For quantitative determination, the HPLC was interfaced with an Agilent 6400 Triple Quadrupole (Agilent, Japan) mass spectrometer (MS/MS). Mass spectrometer was operated with the electrospray ionization (ESI) negative mode. Analyte ions were monitored by using multiple reaction monitoring (MRM) mode. The analytical parameters of each PFC are shown in Table 4.3.

4.4.4 Calibration and Validation

The calibration curves for quantification, consisting of seven points covering from 0.05 to 25 µg/L, generally provided linearity with determination coefficients (R^2) more than 0.999 in every compound. Limit of detection (*LOD*) for HPLC/MS/MS was defined as concentration with signal to noise ratio (*S/N*) equal to 3:1. Practically, *LOQ* was used for quantifying analyte, which was defined by *S/N* 10:1 (Saito *et al.*, 2003; Hansen *et al*., 2002), (Table 4.3). The duplicated analysis was also performed on all samples and coefficients of variations (*CV*) of concentrations were below 20%. During the samples collection and analysis, analytical blanks were performed by using *ultrapure* water. PFCs concentrations were less than the *LOQ*, indicating no contamination during the process.

4.5 Method Accuracy and Matrix Interferences

The recovery rates were calculated by spiking PFCs standards into duplicated samples before LC-MS/MS analysis. The average recovery range was 5% – 131% for aqueous phase and 40% – 116% for particulate phase. Table 4.4 shows the results of recovery rates *(aqueous phase)* in influent, aeration tank, effluent, and tap water samples from WWTPs and wastewater effluents from industries in different IZs (IZ1 – IZ10).

Recovery rates of the tap water samples were ranged from 55% – 101%; those of PFPA, PFHxA, and PFHpA were relatively low, at 55% – 81%, when comparing with other PFCs (93% – 101%).

For the WWTP samples, recovery rates were ranged from 33% – 131%. In wastewater, the matrix components present in the extracted samples have potential to cause ionization suppression or enhancement of PFCs in LC/MS/MS analysis. Recovery rates of aeration tank and effluent samples were slightly lower than tap water indicating that there are some losses by the matrix effects. Furthermore, the influent samples, which have more potential of matrix interferences, showed that recovery rates were much lower than other samples by more than 20%. The recovery rates from industries effluent were in a wide range (5% – 123%) depending on types of industries. The characteristic of the wastewater from each type of industry were unique. Thus, the different matrix interferences affect the recovery rates.

Table 4.4 Analysis recovery of industrial wastewater and tap water *(aqueous phase)*

Samples		*n*	C5-A PFPA	C6-A PFHxA	C7-A PFHpA	C8-A PFOA	C9-A PFNA	C10-A PFDA	C11-A PFUnA	C12-A PFDoA	C6-S PFHxS	C8-S PFOS
WWTP	Influent	12	0.33	0.38	0.60	0.68	0.99	0.82	0.69	0.63	0.90	0.49
	Aeration Tank	12	0.44	0.65	0.88	0.87	1.15	1.00	1.08	0.94	0.99	0.85
	Effluent	12	0.41	0.48	0.71	0.81	1.06	1.18	1.31	1.23	0.93	0.87
	Tap water	12	0.55	0.73	0.81	0.96	0.99	1.02	0.99	1.00	0.93	1.01
Industries	Electronics	7	0.41	0.29	0.50	0.63	0.77	0.71	0.63	0.63	0.58	0.54
	Chemical	3	0.23	0.10	0.33	0.71	1.09	0.93	0.71	0.86	0.66	0.44
	Food	3	0.37	0.51	0.65	1.00	0.95	1.03	0.53	0.49	0.83	0.57
	Plastic	4	0.71	0.54	0.64	0.65	0.85	0.83	0.96	0.73	0.83	0.99
	Coating	2	0.46	0.66	0.94	0.95	1.19	1.13	0.69	0.69	1.11	0.06
	Paper	2	0.05	0.06	0.24	0.46	0.64	0.46	0.42	0.51	0.66	0.12
	Textile	2	0.40	0.19	0.94	0.44	1.08	1.23	0.75	0.75	0.75	0.92

These data indicate that the matrix interferences were a major concern in PFCs analysis for wastewater samples. Development of PFCs analysis method in industrial wastewater samples was necessary to overcome the difficulty in analysis for better results. Method development for PFCs analysis is discussed in Chapter 5.

4.6 Occurrences of PFCs in Industrial Zones

4.6.1 PFCs Concentrations in Central Wastewater Treatment Plant

Surveys were conducted in the selected ten industrial zones. Tap water samples were collected to identify the background PFCs level entering into the industries. Effluents and RO samples were collected to determine PFCs released from industrial activities. Table 4.5 shows PFCs concentration in tap water, influent, effluent, and RO samples of selected ten industrial zones. All PFCs were detected in most samples above *LOQ*. The total PFCs concentrations in tap water were ranged from 2.2 to 76.4 ng/L.

PFCs concentrations in tap water were quite different from each IZ because the sources of tap water were either from the lake or reservoir near to each IZ. There is a water treatment plant in each industrial zone providing tap water for all industries inside. The geometric mean of all ten PFCs concentration in tap water was found at 11.8 ng/L. This tap water is used for the workers of IZs for their daily life activities and for the industrial processes. Relative abundance of PFCs in relation to total PFCs in tap water, influent and effluent samples are given in Figure 4.2. PFOS, PFOA, and PFPA were the major PFCs in tap water, accounting for average of 42%, 23%, and 14%, respectively, while other PFCs were less than 10%. The relative enhancement of PFPA in tap water is reliable result comparing with relative abundance in surface water (Section 3.5.1, Chapter 3).

Effluent of each industry inside the IZ was discharged to central WWTP facility. The wastewaters from different types of industries were mixed in equalization tank before entering the biological processes. The process was different in each industrial zone as described in Table 4.1. The influent samples were collected after the equalization tank in each industrial zone. Total PFCs concentrations were ranged from 39.6 to 3,344.1 ng/L. The elevated concentrations were found to be in IZ2 and IZ5 accounting for 1,812.6 ng/L and 3,344.1 ng/L, respectively. PFOS and PFOA were the predominant PFCs with 53% and 30%, respectively.

Table 4.5 PFCs concentrations in tap water, influent, and effluent of central WWTP in industrial zones

Industrial Zone	Type	PFCs concentration (ng/L±SD)									
		C5-A	C6-A	C7-A	C8-A	C9-A	C10-A	C11-A	C12-A	C6-S	C8-S
		PFPA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFDoA	PFHxS	PFOS
IZ1[a]	Tap	ND	1.9	1.7	22.1	1.9	0.7	0.4	0.5	4.0	43.1
	Influent	2.9±4.1	3.3±1.7	3.2±1.6	121.3±142.1	3.5±2.3	1.3±0.3	0.6±0.6	1.0±0.0	2.6±2.6	158.7±149.9
	Effluent	14.2±4.5	4.7±1.8	2.0±0.9	48.3±54.6	2.0±0.5	1.19±0.1	0.6±0.1	0.6±0.1	4.8±1.3	93.6±25.2
IZ2[b]	Tap	0.5±0.5	<LOQ	<LOQ	1.1±1.3	<LOQ	<LOQ	<LOQ	<LOQ	ND	<LOQ
	Influent	66.6±76.6	325.7±153.2	63.2±22.2	1014.1±1212.3	34.0±16.5	94.8±98.2	1.9±0.9	3.9±1.3	3.9±0.6	204.7±276.4
	Effluent	61.0±63.6	324.8±132.7	74.5±33.1	937.8±1103.3	35.4±3.4	147.3±10.1	5.6±0.8	5.5±1.6	3.3±0.5	130.3±75.0
IZ3	Tap	4.2	1.4	0.8	<LOQ	<LOQ	ND	<LOQ	ND	ND	0.3
	Influent	1.1	5.3	2.4	14.6	6.4	ND	0.2	ND	7.9	1.7
	Effluent	7.7	12.5	19.3	57.4	14.7	17.8	1.6	ND	23.6	1.4
IZ4	Tap	1.5	1.3	1.9	7.6	0.6	0.5	0.9	0.4	<LOQ	5.9
	Influent	45.9	14.8	14.2	101.0	5.3	10.5	9.2	24.7	2.2	91.2
	Effluent	36.5	12.4	10.1	91.6	5.1	9.7	8.0	5.6	38.3	131.5
IZ5[c]	Tap	1.6±2.2	<LOQ	1.1±1.0	2.7±2.5	3.6±2.2	0.4±0.6	1.2±0.4	<LOQ	<LOQ	38.2±24.6
	Influent	3.25±36.8	12.0±11.8	9.5±11.0	69.4±81.1	161.5±201.8	6.2±8.7	27.7±35.3	2.8±3.9	27.9±25.8	2994.8±3515.8
	Effluent	35.1±0.6	11.0±8.6	10.3±10.8	85.7±81.2	272.7±138.1	7.4±9.0	196.6±77.8	3.4±4.8	31.4±25.0	5672.9±6103.2
	RO Effluent	4.8±4.7	0.7±0.7	1.0±1.1	1.3±1.2	7.7±5.5	0.4±0.6	1.3±0.1	0.3±0.4	<LOQ	40.9±5.1
IZ6	Tap	4.1	2.0	1.0	12.8	<LOQ	<LOQ	<LOQ	<LOQ	2.0	21.8
	Influent	6.7	8.1	10.7	105.0	1.75759137	ND	0.84733785	ND	1.5	50.0
	Effluent	10.0	10.9	16.9	242.6	5.4	3.1	1.9	<LOQ	4.3	104.1
IZ7	Tap	ND	ND	ND	ND	ND	ND	ND	ND	ND	8.2
	Influent	74.1	ND	ND	70.9	ND		ND		ND	34.5
	Effluent	ND	ND	ND	86.0	12.7	24.7	ND	ND	ND	12.7
IZ8	Tap	2.0	ND	ND	1.4	<LOQ	ND	ND	<LOQ	ND	0.9
	Influent	15.9	5.4	2.4	15.7	3.62195179	0.5	ND	ND	11.7	152.2
	Effluent	5.8	3.3	2.9	21.8	3.0	<LOQ	<LOQ	ND	3.0	37.4
IZ9[d]	Tap	ND	ND	ND	1.9	1.1	ND	ND	ND	ND	ND
	Influent	0.1±0.1	4.4±3.8	11.4±18.1	579.2±902.1	7.6±8.2	4.9±6.8	0.5±0.9	ND	ND	64.0±100.6
	Effluent	7.0±3.0	2.3±4.1	12.9±17.0	316.3±353.7	10.1±9.8	8.5±7.7	1.5±0.8	ND	1.2±2.0	18.6±20.5
IZ10	Tap	ND	ND	<LOQ	<LOQ	0.2	NA	0.1	ND	1.4	8.8
	Influent	ND	3.4	3.9	8.9	1.3	0.7	ND	1.8	7.5	8.1
	Effluent	ND	4.0	8.5	9.7	2.5	0.8	ND	0.4	37.7	63.3

Note: ND = Not detected (Lower than Limit of detection), <LOQ = lower than Limit of Quantification

[a]Three phases of wastewater treatment plant (AS and two wetlands)

[b]Repeated sampling was conducted due to high PFCs concentration

[c]Repeated sampling was conducted due to high PFCs concentration and included advanced processes (sand filtraion, MF, and RO)

[d]Two phase of wastewater treatment plant (AS and RBC)

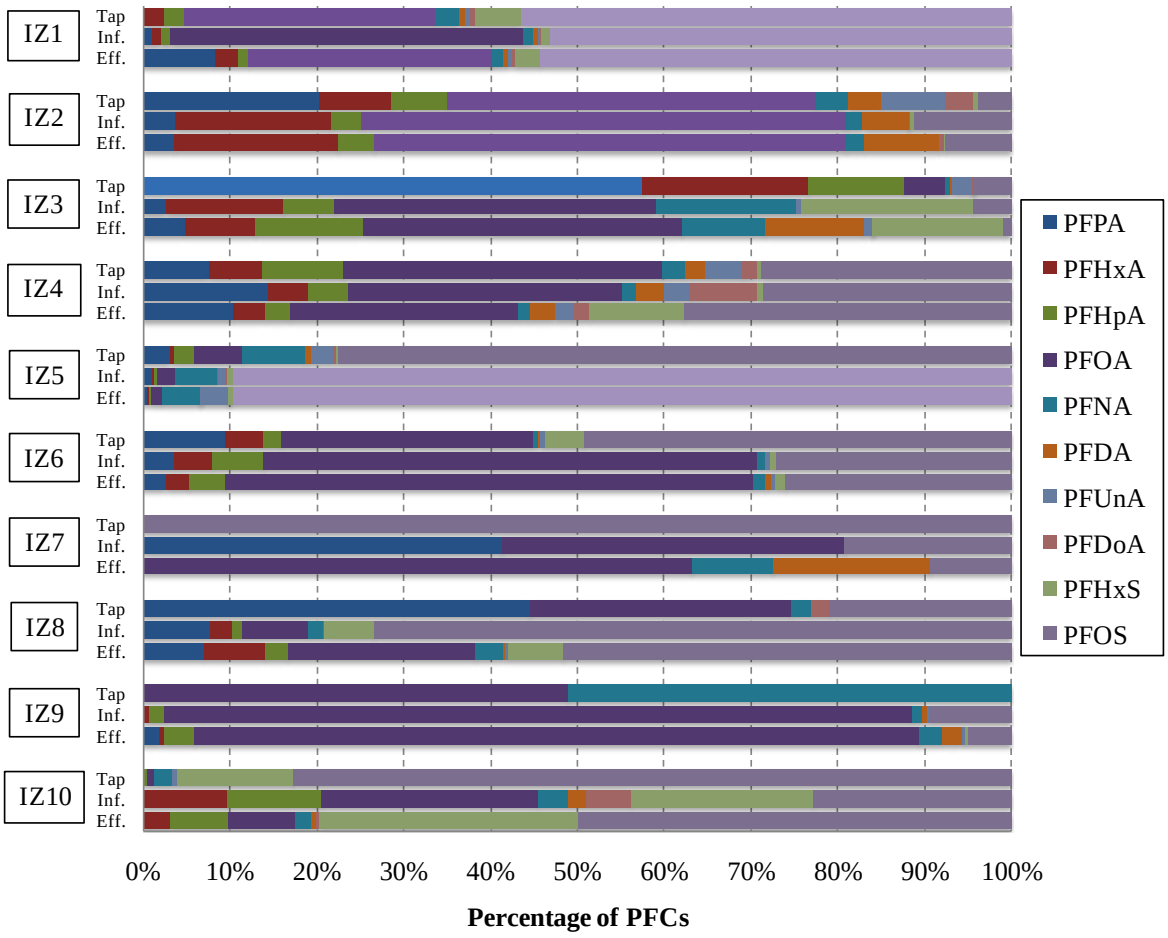


Figure 4.2 Relative abundances of PFCs in tap water, influent and effluent of WWTP

PFCs concentrations in effluent samples were varied from 94.3 to 6326.5 ng/L. The geometric mean combined PFCs in the effluent was at 346.8 ng/L. The elevated concentrations (>1000 ng/L) were found in IZ2 and IZ5, accounting for 1725.5 ng/L and 6326.5 ng/L, respectively. These two IZs released 82% of total PFCs discharged by ten IZs. Due to the elevated PFCs concentration in IZ2 and IZ5, the repeated samplings were conducted in these two industrial zones to identify reproducibility of these compounds.

The major PFCs found in IZ2 were PFOA, PFHxA, PFDA, and PFOS, accounting for 54%, 19%, 9%, and 8% of total PFCs, while in IZ5 only PFOS was the dominant PFCs with 90% (Figure 4.2). The results indicated that relative abundance of PFCs in the IZs were different

between places. It was not related with the number of industries (IZ9 was the highest) or amount of the wastewater (IZ1 was the highest) among the IZs (Table 4.1). There are specific types of industry that use these compound in their industrial applications such as electronics, chemicals, plastic, glass, surface coating, and personal care products. In fact, two big fluorinated compounds manufacturers are locate in IZ5, while there are many electronics and chemicals companies located in IZ2. The sources of PFCs contamination might actually be coming from these industries.

4.6.2 PFCs Concentrations from Industries in Industrial Zones

The effluents of different types of industries were collected to identify the possible source of PFCs contamination. Samples were collected from IZ2, IZ3, IZ4 and IZ8, while we could not get the permission in other industrial zones. Selected types of industries that have potentials to release PFCs, were electronics, plastic, air-condition making, chemicals, material coating, glass making and textile industries. The samples also collected from effluent of food making factory, which were likely the non-PFCs related industry to compare the PFCs concentration.

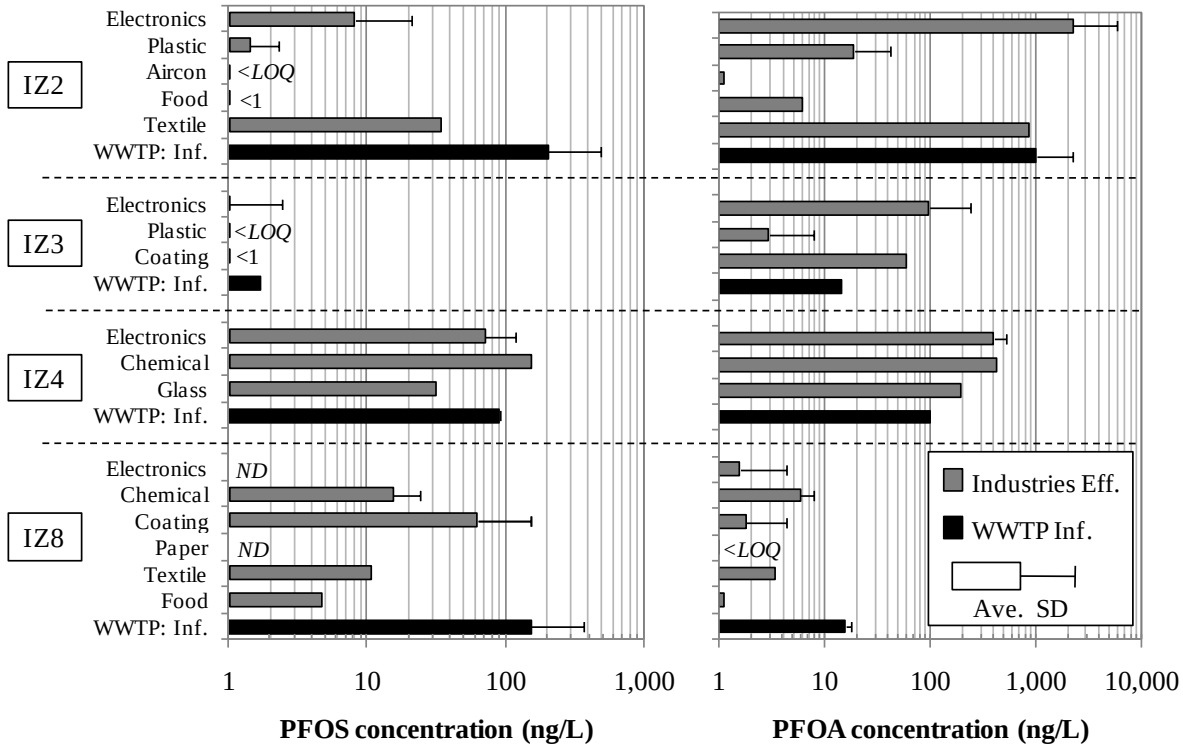
Table 4.6 presents the PFCs concentrations in effluents of the industries inside industrial zones. Total PFCs concentrations were ranged from 8.6 ng/L to 3,434.7 ng/L with the geometric mean of 99.4 ng/L. The elevated concentration (>800 ng/L) were detected in electronics, textile, chemicals and glass making industries. The highest concentration was detected at one of the electronics industries in IZ2. Effluents from food industries contained the lowest PFCs concentrations, 8.6 ng/L in IZ8 and 11.0 ng/L in IZ2. The result confirmed that the food productions were not related with PFCs.

Figure 4.3 illustrates the influence of PFOS and PFOA concentrations from different industries to influent of industrial zones' WWTP. In IZ2, electronics and textile industries were one of the major sources of PFOS and PFOA discharging to WWTP. PFOA concentrations in the effluents of electronics industry were higher than the WWTP influent. PFOA was the predominant PFCs releasing from IZ3. The selected electronics and coating industries were also one of the major sources of the PFOA contamination.

Table 4.6 PFCs concentrations in effluents of the industries inside industrial zones

Industrial Zone	Type of Industry	*n*	PFCs concentration (ng/L±SD)									
			C5-A	C6-A	C7-A	C8-A	C9-A	C10-A	C11-A	C12-A	C6-S	C8-S
			PFPA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFDoA	PFHxS	PFOS
IZ2	Electronics	3	88.7±80.4	703.6±945.0	169.2±218.7	2236.2±3644.0	84.3±87.8	129.0±206.3	7.0±11.0	7.5±9.5	1.0±1.1	8.1±12.5
	Plastic	2	6.6±3.1	1.2±0.8	0.9±0.2	18.9±22.3	0.8±1.1	1.3±1.9	0.3±0.3	<LOQ	<LOQ	1.4±0.9
	Aircon	1	24.4	0.8	0.4	1.0	ND	ND	0.6	ND	ND	<LOQ
	Food	1	0.7	<LOQ	0.7	6.1	0.5	0.6	<LOQ	0.4	1.3	0.4
	Textile	1	5.4	66.3	34.9	855.4	17.6	47.3	0.8	0.4	2.8	34.1
IZ3	Electronics	4	54.7±96.2	7.4±8.7	2.9±2.3	96.3±146.9	29.2±41.1	22.5±25.2	6.5±8.0	2.4±3.0	0.6±0.6	1.0±1.5
	Plastic	3	76.7±64.8	2.0±1.4	0.5±0.6	2.9±4.8	0.5±0.4	0.3±0.4	<LOQ	<LOQ	0.7±0.9	<LOQ
	Coating	1	1.0	1.8	2.4	60.0	1.3	1.2	<LOQ	ND	0.4	0.8
IZ4	Electronics	2	127.1±34.3	84.6±25.7	145.2±52.5	395.3±133.6	105.7±33.9	82.4±13.5	57.8±8.3	68.6±8.2	51.4±5.6	70.6±48.4
	Chemical	1	68.5	109.3	174.5	425.2	119.9	86.1	57.9	68.5	54.9	155.8
	Glass	1	84.7	88.5	79.3	193.3	65.4	71.3	54.9	101.8	37.9	31.1
IZ8	Electronics	3	1.2±1.8	13.9±24.0	ND	1.6±2.7	11.8±20.0	ND	1.0±1.8	<LOQ	ND	ND
	Chemical	2	19.0±26.9	2.7±3.8	ND	5.9±2.0	1.7±0.1	ND	ND	ND	3.2±4.5	15.2±9.1
	Coating	2	0.4±0.5	1.0±1.3	0.5±0.7	1.8±2.5	0.6±0.7	ND	ND	ND	ND	62.6±88.5
	Paper	2	9.1±12.0	2.5±3.5	ND	<LOQ	<LOQ	ND	ND	ND	ND	ND
	Textile	1	ND	ND	ND	3.4	1.5	ND	ND	ND	ND	10.6
	Food	1	ND	ND	ND	1.0	0.7	ND	ND	ND	2.3	4.7

Note: ND = Not detected (Lower than Limit of detection), <LOQ = lower than Limit of Quantification



Note: <*LOQ* = Less than Limit of Quantification, ND = Not Detected

Figure 4.3 PFOS and PFOA concentration from different industries inside industrial zones

In contrast, industries in this IZ3 were detected low PFOS contamination in the samples, indicating that there is less PFOS related activities in this industrial zone. Electronics, chemical, and glass making companies inside IZ4 were clearly indicate that they were the sources of PFCs in the area. In IZ8, PFOS was the predominant PFCs. Coating industry in this zone was the major source of PFOS, unlike the coating industries in IZ3, where PFOA is the predominant. From the result, it might be indicated that electronics industries was the major source of PFCs contamination. However, the PFCs discharges were different even from the same type of industry. Thus, the sampling is important to identify the sources of PFCs in the area.

4.6.3 Loading of PFCs Released from Industrial Zones

Table 4.7 shows PFCs loading discharges from ten IZs. WWTPs discharge flow rate is shown in Table 4.1. Ten industrial zones released 188.41 g/d of PFCs. PFOS, PFOA, and PFNA were the dominant compounds releasing from the IZs with the loadings of 125.58 g/d (67%), 34.35 g/d (18%), and 7.25 g/d (4%), respectively. Mainly, IZ5 was discharging PFCs that alone contributed 91% of all PFOS loadings and 77% PFNA of total discharges. IZ2, IZ9, and IZ6 were discharging PFOA with the loadings 11.25 g/d, 9.14 g/d, and 5.75 g/d, respectively.

Table 4.7 PFCs loading from industrial zones

Industrial Zones	PFCs loading (g/d)										
	PFPA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFDoA	PFHxS	PFOS	Ten PFCs
IZ1	0.43	0.14	0.06	1.45	0.06	0.04	0.02	0.02	0.14	2.81	5.16
IZ2	0.73	3.90	0.89	11.25	0.42	1.77	0.07	0.07	0.04	1.56	20.71
IZ3	0.13	0.21	0.32	0.96	0.25	0.30	0.03	<0.01	0.40	0.02	2.62
IZ4	0.51	0.17	0.14	1.28	0.07	0.14	0.11	0.08	0.54	1.84	4.88
IZ5	0.70	0.22	0.21	1.71	5.45	0.15	3.93	0.07	0.63	113.46	126.53
IZ6	0.24	0.26	0.40	5.75	0.13	0.07	0.04	<0.01	0.10	2.47	9.46
IZ7	ND	ND	ND	2.24	0.33	0.64	ND	ND	ND	0.33	3.54
IZ8	0.14	0.14	0.05	0.43	0.07	<0.01	0.01	ND	0.13	1.02	1.98
IZ9	0.20	0.07	0.37	9.14	0.29	0.25	0.04	ND	0.03	0.54	10.94
IZ10	ND	0.04	0.09	0.11	0.03	0.01	ND	<0.01	0.42	0.71	1.42
Total	3.08	5.15	2.55	34.33	7.10	3.35	4.25	0.23	2.43	124.76	187.24

Figure 4.4 shows the PFCs loading in tap water, influent and effluent samples in ten industrial zones. The number (loading, g/d) in the graph is equal to PFCs loading in influent of WWTP minus PFCs in tap water samples, presenting the amount of PFCs generated from the industrial activities. IZ5 and IZ2 were among the major industrial zones that highly generated PFCs with 21.7 g/d and 65.7 g/d, respectively. In fact, tap water was also one of the sources of PFCs discharged in WWTP, for instance, PFCs in the tap water of IZ1 accounted for 31% of the PFCs concentration in the influent. PFCs contaminations in tap water in most samples were from the discharges of PFCs in the same industrial zone, because most of the IZs use nearby surface water resources for daily production. Figure 4.4 also shows that PFCs in the effluents of IZ3 to IZ8 was

increasing, when PFCs in tap water was also increasing. Moreover, the different loading between influent and effluent samples of WWTP was indicated as the combination of PFCs removal and transformation of the precursors inside the wastewater treatment processes. WWTP in most industrial zones were shown the difficulty in removing PFCs.

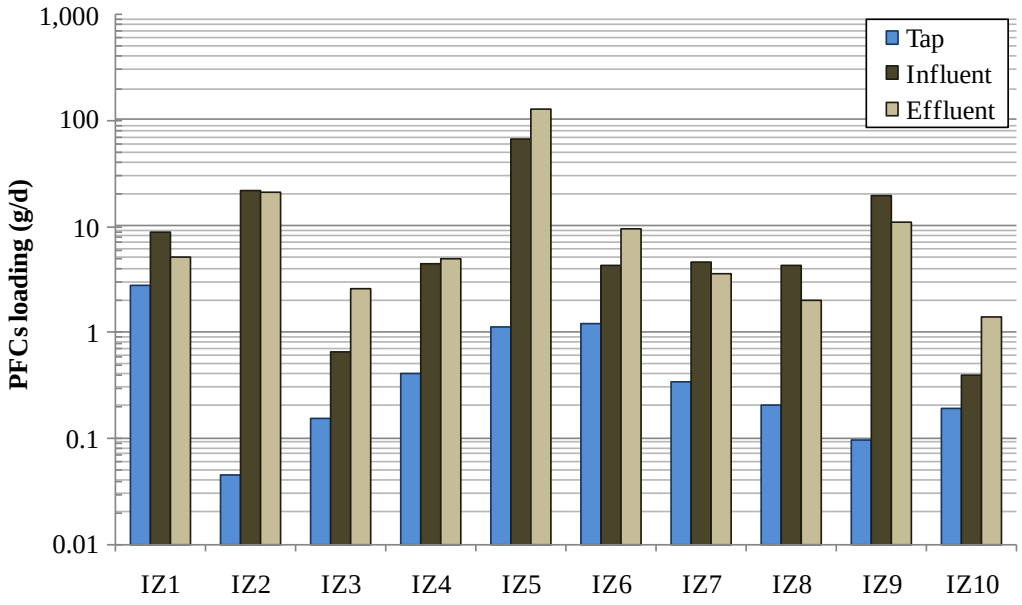


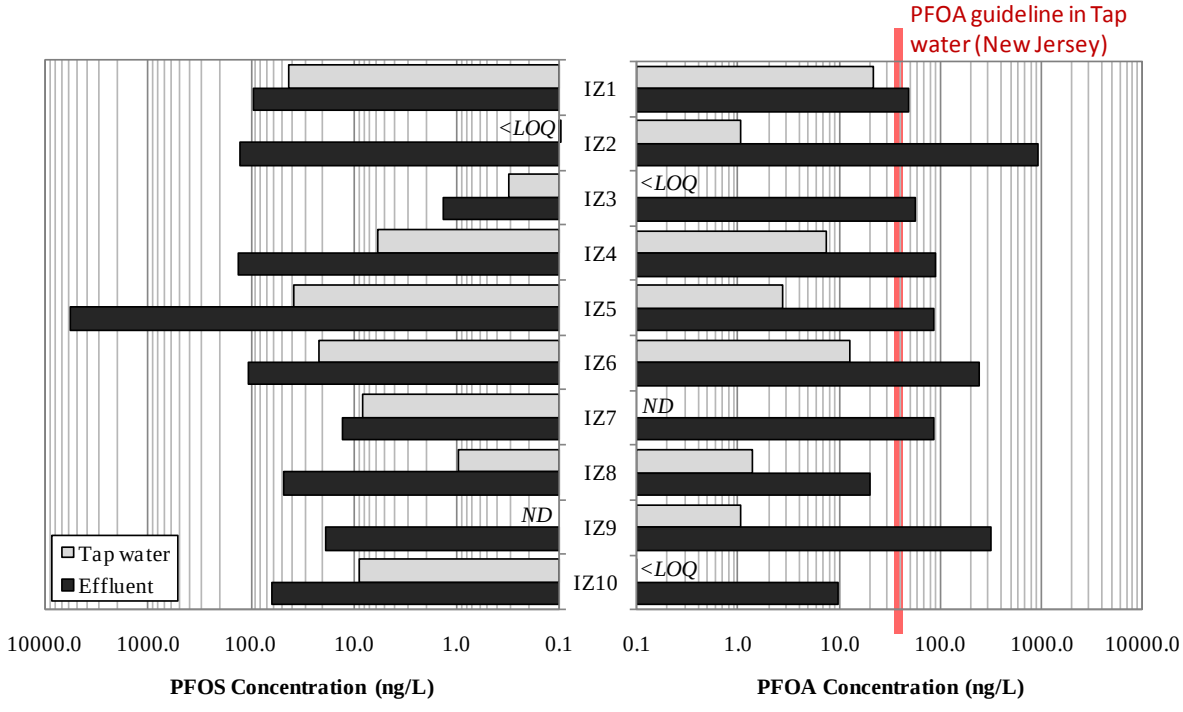
Figure 4.4 PFCs loadings in industrial zones

4.6.4 PFOS and PFOA Concentrations

Figure 4.5 shows the PFOS and PFOA concentration in tap water and effluent samples in the industrial zones. PFOS were detected in most samples except tap water in IZ2 and IZ9. PFOS was the dominant PFC in five industrial zones (IZ1, IZ4, IZ5, IZ8, and IZ10) (Figure 4.2). PFOS concentrations were varied from *ND* – 43.1 ng/L (GM = 2.9 ng/L) in tap water and 1.4 – 5672.9 ng/L (GM = 62.7 ng/L) in effluent. The highest PFOS was detected in IZ5, which received wastewater from two PFCs manufacturers. Effluents from the industries inside IZs are the combination of wastewater from the industrial processes and also from the domestic activities such as toilet and restaurant usages. The highest concentration of PFOS determined here was much higher than in municipal wastewater treatment plant reported in U.S.A. (Sinclair and Kannan, 2006), Singapore (Yu *et al.*, 2009), Switzerland (Huset *et al.*, 2008), and Japan (Lien, *et al.*, 2008).

However, the range of PFOS concentrations releasing from different industrial zones was much wider. Much lower concentrations (<100 ng/L) of PFOS were found in other six IZs (IZ1, IZ3, IZ7, IZ8, IZ9, and IZ10). One possible interpretation on difference of PFOS concentrations from IZs is the different in types of industries and usages of PFOS in each IZ.

Concentrations of PFOA were greater in the effluent of five industrial zones (IZ2, IZ3, IZ6, IZ7, and IZ9) (Figure 4.2). PFOA range in tap water and in effluent were *ND* – 22.1 ng/L (GM = 1.2 ng/L) and 9.7 – 937.8 ng/L (GM = 87.6 ng/L), respectively. The highest PFOA was found at IZ2 with concentration of 937.8 ng/L. PFOA concentrations are comparable to those measured in municipal WWTPs in New York State, USA (Sinclair and Kannan, 2006). However, it does not mean that PFOA were not released from the industrial activities. PFOA concentration levels among countries are not similar, for instance, in Section 3.7 (Chapter 3), the PFOA level in surface water (major rivers) was much less than in Osaka (Japan). The comparison of municipal wastewater and industrial wastewater was needed for better understanding of PFCs contamination from industrial activities.

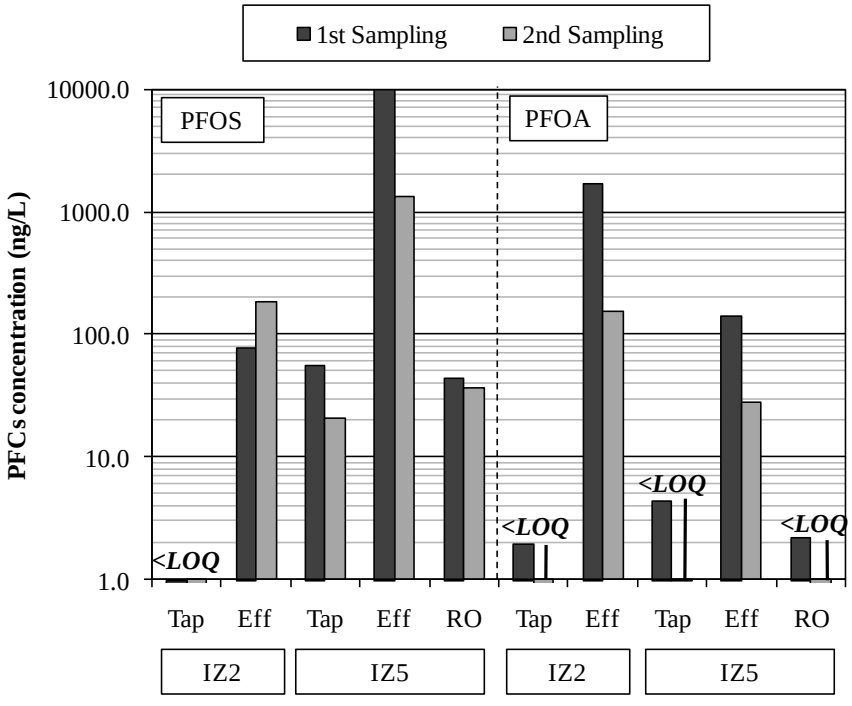


Note: ND = Not Detected, <LOQ = Less than Limit of Quantification, Tap = Tap water, Eff. = Effluent

Figure 4.5 PFOS and PFOA concentration discharge from industrial zones

4.6.5 Repeated Sampling in IZ2 and IZ5

Repeated samplings were performed in the industrial zones IZ2 and IZ5, where the elevated concentration of PFOS and PFOA, were detected in the first sampling to identify the reproducibility of PFOS and PFOA. Figure 4.6 shows the comparison of PFOS and PFOA concentrations in first and second sampling. Both PFOS and PFOA were detected in most samples during first and second sampling. This provides evidence that PFOS and PFOA are still released into receiving surface waters. However, PFCs were detected in lower concentration during the second sampling in eight out of ten samples. PFOS concentrations were decreasing in the second sampling with the average 56%. The declining of PFOS released might be from the phase-out of PFOS from a PFCs manufacturer. The recent studies have also shown declining concentration of PFOS in environmental, and blood samples (Tagaki *et al*., 2008; Renner, 2008); however, very high concentration of PFOS detected in effluent of IZ5 might indicate its significant application in Thailand.



Note: <*LOQ* = Less than Limit of Quantification

Figure 4.6 Comparison of PFOS and PFOA concentrations in repeated sampling

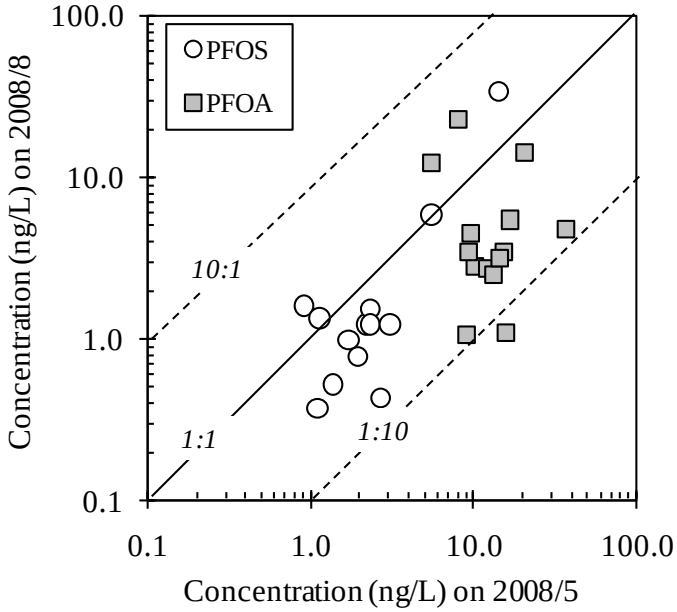


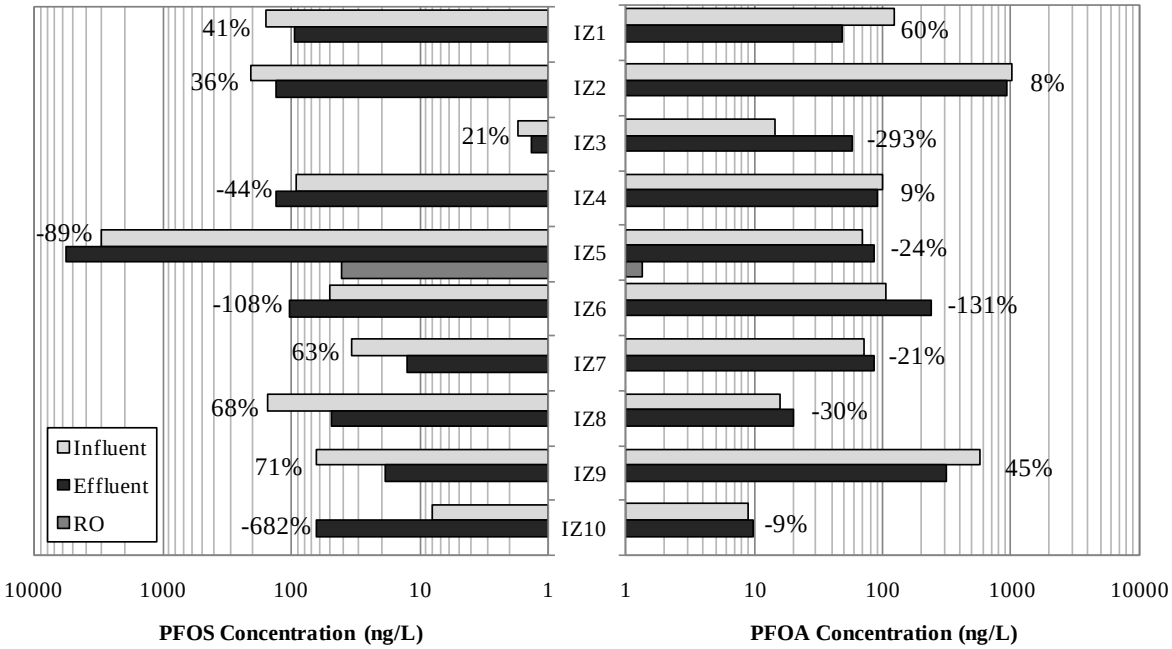
Figure 4.7 Comparison of PFOS and PFOA concentration in Chao Phraya River on 2008/5 and 2008/8

The decreasing in PFOA concentrations were also found in all samples with the average 84%. The similar result on the decreasing of PFOS and PFOA detection in Chao Phraya River in 2008 was shown in Figure 4.7. The figure shows the comparison of PFOS and PFOA concentration in Chao Phraya River on 2008/5 and 2008/8. Most of the plots were below linear line 1:1 indicating that the PFCs concentration in 2008/8 was lower than in 2008/5. It can be concluded that the decreasing PFOS and PFOA concentrations in industrial wastewater also had an effect in the concentration of surface water.

4.6.6 Performance on Removal of PFCs in Central Wastewater Treatment Plant

Figure 4.8 illustrates the PFOS and PFOA concentrations in influent, effluent and RO samples in WWTP. The percentage showed in the chart indicates the removal percentage in each WWTP. All of the treatment processes inside industrial zones were biological processes as described in Table 4.1. The conventional activated sludge process was used in the nine out of ten industrial zones. Most treatment processes were not effective to remove PFOS and PFOA. PFOS removal percentages were ranged from

-682% to 71%, while PFOA removal percentages ranged from -293% to 60%. The increasing PFOA concentration in the effluent was also found in seven domestic WWTP (Schultz *et al.*, 2006). Previous studies also showed that biological processes were not shown any significant removal of PFCs (Boulanger *et al.*, 2005 and Sinclair and Kannan, 2006).

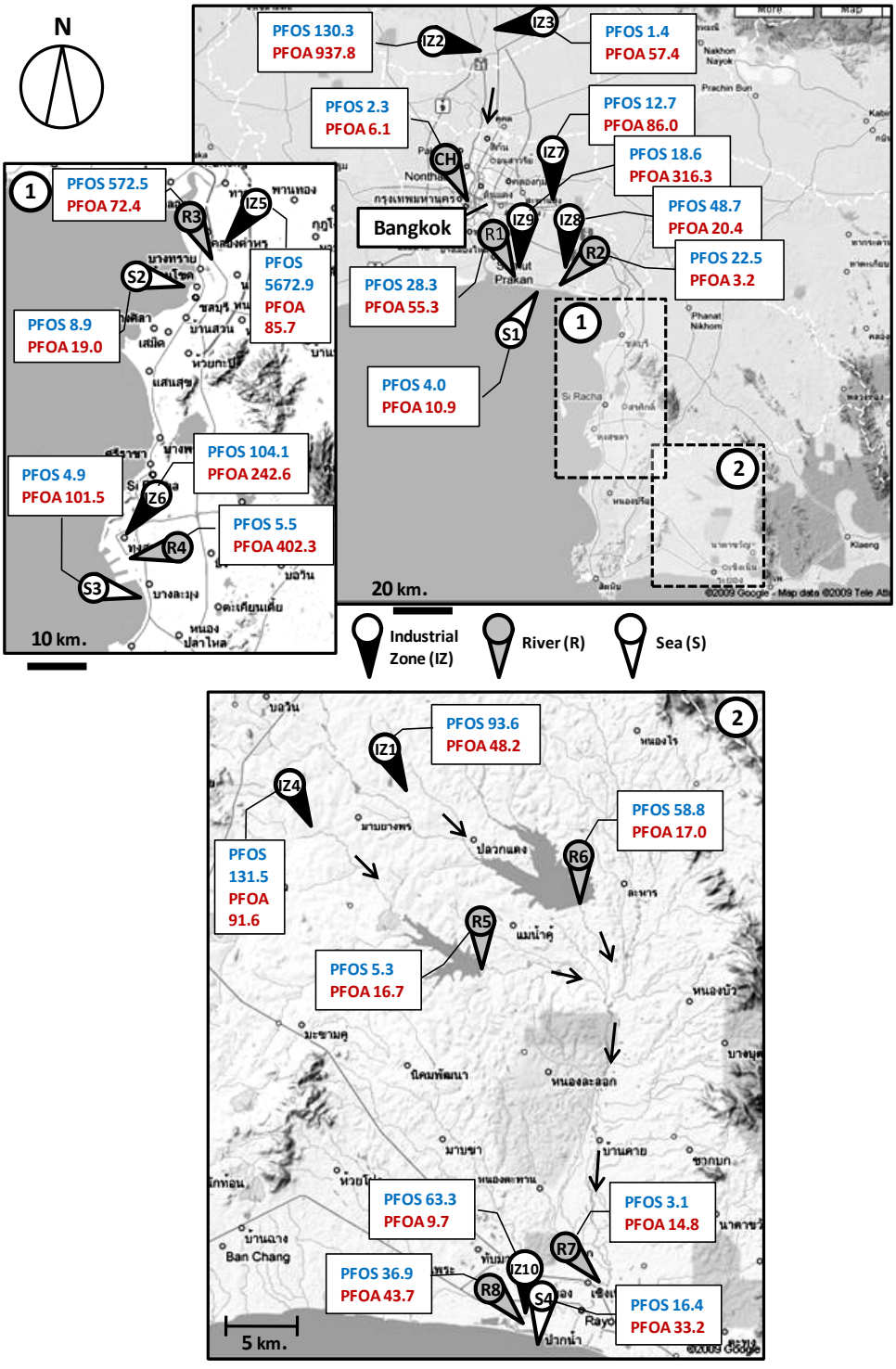


Note: ND = Not Detected, <LOQ = Less than Limit of Quantification, Tap = Tap water, Eff. = Effluent, RO = Reverse Osmosis

Figure 4.8 PFOS and PFOA concentrations in influent, effluent and RO samples in WWTP

However, there is an advanced treatment process in the central WWTP in IZ5. Sand filtration, microfiltration (MF) and reverse osmosis (RO) processes are used for treating effluent from Sequencing Batch Reactor (SBR). The product water from RO process is used in power plant inside the industrial zone. Tang *et al*. (2006) reported that RO membrane is effective for removing PFCs from semiconductor wastewater in the pilot scale. The result from this study also showed that RO process was effective to remove PFCs in the real scale application. Advanced processes in the IZ5 can remove PFOS and PFOA by 99.3 and 98.5%, respectively.

4.7 Influence of PFOS and PFOA Discharge from Industrial Zones to nearby Surface water



Source: Google Maps

Figure 4.9 PFOS and PFOA concentrations (ng/L) in industrial effluents and surface water

Figure 4.9 shows PFOS and PFOA concentrations in industrial effluents comparing to nearby surface water from the study in Chapter 3. From Chapter 3, it suggested that the industrial effluents might be the source of PFCs contamination in environmental water. The result from this chapter was confirmed the contamination. Most of the industrial discharges from the industrial zones were the influence of PFCs contamination in the surface water in the lower reach of each industrial zone. Comparing to industrial discharges, the lower PFCs ranges in the rivers and reservoirs were detected due to the dilution in the surface water. The dilution factor was important to the PFCs level detected in the surface water. For example, even the high PFOA was detected in IZ2 (937.8 ng/L), low concentration was detected in Chao Phraya River (6.1 ng/L). Comparing to small river, for instance, PFOS concentration detected in IZ5 (5,672.9 ng/L) and R3 (572.5 ng/L) in the lower reach of the industrial zone. The influence of industrial discharges was affected not only the rivers and reservoirs but also in the coastal water. The higher ranges of PFCs were also detected in the coastal water, where high range of PFCs detected in the industrial zone nearby.

4.8 Summary

Field surveys were conducted in ten industrial zones. Influent, aeration tank, and effluent samples were collected from central wastewater treatment plants of each industrial zone. Effluent samples from selected industries were also collected. Tap water samples were also collected to identify the background concentration of the industrial zones. The recovery rates indicated that the matrix interferences were a major concern in PFCs analysis. Development of PFCs analysis method in industrial wastewater samples was necessary to overcome the difficulty in analysis for comprehensive results.

All PFCs were detected in most samples above *LOQ*. The combined ten PFCs concentrations in tap water were ranged from 2.2 to 76.4 ng/L. PFCs concentrations in tap water were quite different from each zone because the sources of tap water were either from the lake or reservoir nearby each industrial zone. The wastewaters from different types of industries were mixed in equalization tank before entering the biological processes. The elevated concentration was detected in electronics, textile,

chemicals and glass making industries. The highest concentration was detected at one of the electronics industries in IZ2, while the lowest was found in food industry.

Total PFCs concentrations in the influent of WWTP were ranged from 39.6 to 3,344.1 ng/L. The elevated concentrations were found in IZ2 and IZ5 accounting for 1,812.6 ng/L and 3,344.1 ng/L, respectively. The major PFCs found in IZ2 were PFOA, PFHxA, PFDA, and PFOS, accounting for 54%, 19%, 9%, and 8% of total PFCs, while in IZ5 only PFOS was the dominant PFCs with 90%. Ten industrial zones released 188.41 g/d of PFCs. PFOS, PFOA, and PFNA were the dominant compounds releasing from the industrial zones with the loadings 125.58 g/d (67%), 34.35 g/d (18%), and 7.25 g/d (4%), respectively.

All of the treatment processes inside industrial zones were biological processes. Most treatment processes were not effective to remove PFOS and PFOA. However, the result from this study also showed that RO process was effective to remove PFCs in the real scale application. Advanced processes in the IZ5 can remove PFOS and PFOA by 99.3 and 98.5%, respectively.

Repeated samplings were performed in the industrial zones IZ2 and IZ5, where the elevated concentration of PFOS and PFOA, were detected in the first sampling to identify the reproducibility of PFOS and PFOA. Both PFOS and PFOA were detected in most samples during the first and second sampling. This provides evidence that PFOS and PFOA are still released into receiving surface waters. Comparing to trend of PFCs in surface water, it can be concluded that the decreasing PFOS and PFOA concentrations in industrial wastewater also had an effect in the concentration of surface water. The influence of industrial discharges not only affected the rivers and reservoirs but also in the coastal water. The higher ranges of PFCs were also detected in the coastal water, where high range of PFCs detected in the industrial zone nearby.

Chapter 5

Development of Perfluorinated Compounds Analysis Method in Water and Wastewater Samples

5.1 Introduction

The method development of PFCs analysis in environmental samples has been a major focus for many years (Hansen *et al.*, 2001). In general, solid phase extraction (SPE) coupled with LC-MS/MS is used to analyze PFCs in environmental matrices. SPE is used for concentrating analytes and removing matrix and inorganic compounds. PresepC-Agri (C18), Oasis®WAX and Oasis®HLB plus was normally used in SPE process for analyzing PFOS and PFOA in environmental samples (Saito *et al.*, 2003; Taniyasu *et al.*, 2005; Lien, 2007). In this study, PresepC-Agri (C_{18}) was performed for analyzing ten PFCs in surface water, tap water, and industrial wastewater as described in Chapter 3 and Chapter 4. The difficulty in analysis of industrial wastewater was noted in Section 4.5, Chapter 4. The ineffective SPE procedure and matrix interferences were the two major difficulties for analyzing environmental water and industrial wastewater samples. Leeuwen *et al.* (2006) also reported the difficulty of determination of PFCs in environmental and human samples. To overcome ineffective in analytical procedure, the optimizing SPE process and matrix removal procedure were needed.

5.2 Objectives

The purposes of the study were to optimize PFCs analysis in surface water samples and industrial wastewater samples and to apply matrix removal method for industrial wastewater samples. In this Chapter, the several options for optimizing SPE were performed such as changing cartridges, changing flow rate of SPE procedure, changing types of solvent, changing solvent volume, and changing solvent percentages.

Moreover, the several matrix removal methods were compared to overcome matrix interferences.

5.3 PFCs Standards

In this study, ten PFCs standards and PFCs mass labeled internal standards ($^{13}C_2$-PFHxA, $^{13}C_4$-PFOA, $^{13}C_2$-PFDA, and $^{13}C_4$-PFOS) were selected as target chemicals. Standard reagents were obtained from Wellington Laboratories, Canada, with purities of >99% (Table 5.1). PFCs stock solution was prepared by dissolving Perfluorocarboxylic acids mixed solution (PFC-MXA) and perfluorosulfonates mixed solution (PFS-MXA) into 100 mL acetronitrile (LC/MS grade) and stored in polypropylene (PP) bottle at 4ºC. PFCs standard solutions were prepared by diluting different volumes of single stock solutions together into 25% acetronitrile solvent. These multi component standard contained same concentration of each PFC.

Table 5.1 PFCs standards used in this study

Compound	Fullname	Molecular weight
PFPA	Perfluoropentanoic acid	263
PFHxA	Perfluorohexanoic acid	313
PFHpA	Perfluoroheptanoic acid	363
PFOA	Perfluorooctanoic acid	413
PFNA	Perfluorononanoic acid	463
PFDA	Perfluorodecanoic acid	513
PFUnA	Perfluoroundecanoic acid	563
PFDoA	Perfluorododecanoic acid	613
PFHxS	Perfluorohexane sulfonate	399
PFOS	Perfluorooctane sulfonate	499
$^{13}C_2$-PFHxA	Mass labelled Perfluorohexanoic acid	315
$^{13}C_4$-PFOA	Mass labelled Perfluorooctanoic acid	417
$^{13}C_2$-PFDA	Mass labelled Perfluorodecanoic acid	515
$^{13}C_4$-PFOS	Mass labelled Perfluorooctane sulfonate	503

PFCs internal standard was separately diluted from normal PFCs standards. $^{13}C_4$-PFOA, $^{13}C_4$-PFOS, $^{13}C_2$-PFHxA and $^{13}C_2$-PFDA were purchased from Wellington Company, Canada. Internal standards were prepared by dissolving into 100 mL acetronitrile

(LC/MS grade) solvent and stored in polypropylene (PP) bottle at 4ºC. Internal standard solutions were prepared by diluting different volumes of single stock solutions together into 25% acetronitrile solvent.

5.4 Conventional PFCs Analysis Method

5.4.1 Sample Preparation and Extraction

Figure 5.1 shows the conventional analytical procedure of PFCs.

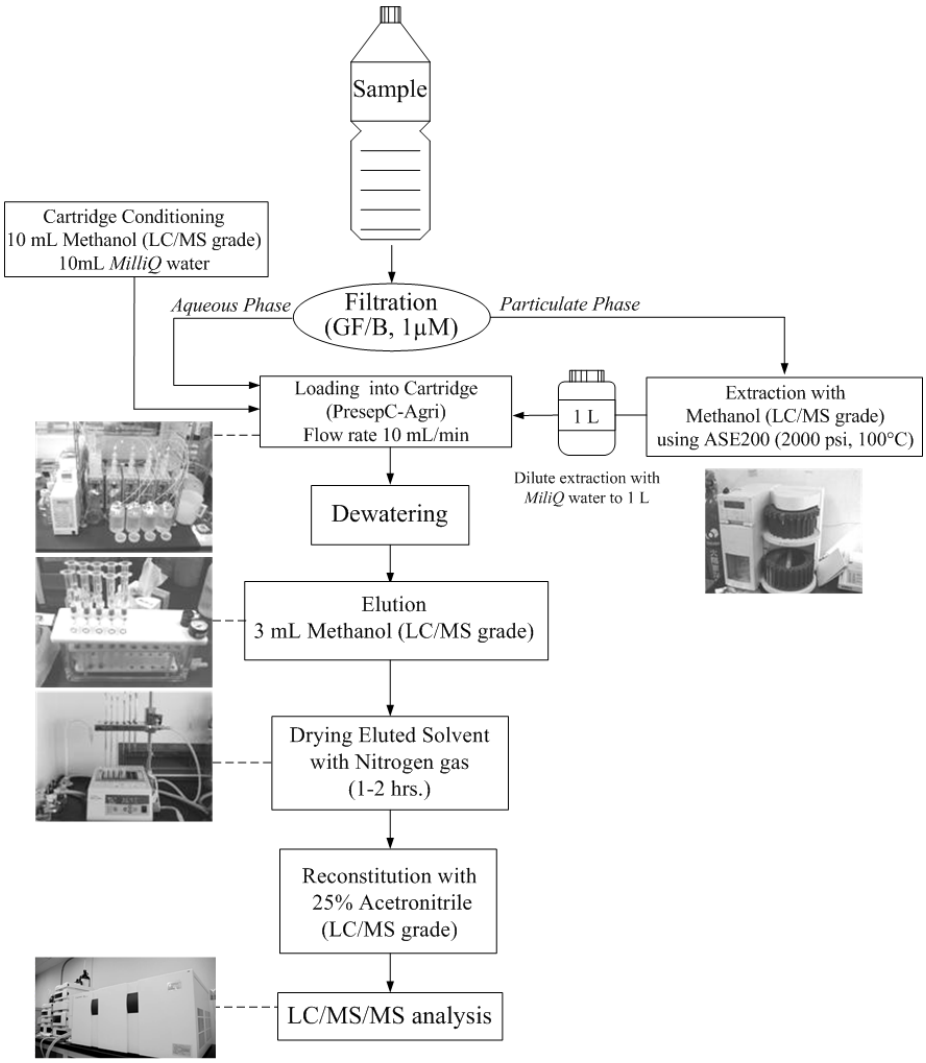


Figure 5.1 Conventional analytical procedure for PFCs

Liquid phase samples: A sample was filtered by 1 µm GF/B glass fiber filter to separate suspended solids. The filter was then further analyzed by using Accelerated Solvent Extraction (ASE-200) from Dionex, Japan. SPE process was used for concentrating PFCs. The filtrate (500 mL) was passed through a PresepC-Agri (C18) cartridge (Wako, Japan) preconditioned by 10 mL of LC/MS-grade methanol followed by 20 mL *Milli-Q* water manually. PFCs standards were spiked (10 ng/L) into a duplicated sample before loading to find their recoveries. A flow rate of 10 mL/min was maintained through the cartridge. The above procedures were completed in Thailand and the cartridges were brought back to Japan for further analysis. In Japan, each cartridge was dried completely under vacuum. Then, the target compounds were eluted with 3 mL LC/MS-grade methanol into a polypropylene tube, evaporated to dryness with nitrogen gas, and reconstituted into LC/MS mobile phase (25% LC/MS-grade acetronitrile) to a final volume 2 mL. PFCs in filtrates were concentrated by a factor of 250 times.

Solid phase samples: The suspended solids part was separated by GF/B filter (Filtered volume: 500 mL). The filters were air dried and inserted to ASE cells (Volume: 33 mL) for extraction. The standard 10 ng/L was spiked into the duplicated cell before extraction. The extraction was done by using Methanol as a solvent. The extraction was run three cycles (15 min per one cycle) by using pressure 2,000 psi and temperature 100ºC. Final extracted volume was 60 – 80 mL. Then, the extracted sample was diluted with LC/MS-grade ultrapure water into 1 L, loaded to a PresepC-Agri (C18) cartridge, and continued with the same procedure as liquid phase samples.

5.4.2 Instrumental Analysis and Quantification

Separation of PFCs was performed by using Agilent 1200SL high-performance liquid chromatography (HPLC), (Agilent, Japan). Extract 10µL was injected to a 2.1×100 mm (5 µm) Agilent Eclipse XDB-C_{18} column. Mobile phase consisted of (A) 5 mM ammonium acetate in *ultrapure* water (LC/MS grade) and (B) 100% Acetronitrile (LC/MS grade). At a flow rate of 0.25 mL/min, the separation process started with initial condition of 30% (B), increased to 50% (B) at 16.5 min, then to 70% (B) at 16.6,

held at 70% (B) for 3.4 min, went up to 90% (B) at 21 min, kept at 90% (B) for 1 min, and then ramped down to 30% (B). The total running time was 34 min for each sample. For quantitative determination, the HPLC was interfaced with an Agilent 6400 Triple Quadrupole (Agilent, Japan) mass spectrometer (MS/MS). Mass spectrometer was operated with the electrospray ionization (ESI) negative mode. Analyte ion monitored by using multiple reaction monitoring (MRM) mode. The analytical parameters of each PFC are shown in Table 5.2.

Table 5.2 Analytical Parameters of PFCs

Compound	No. of Carbon	Parent ion (*m/z*)	Daughter ion (*m/z*)	CE* (eV)	Retention time (min.)	LOD (ng/L)	LOQ (ng/L)
PFPA	C5-A	263	219	5	1.9	0.02	0.05
PFHxA	C6-A	313	269	5	2.8	0.01	0.02
PFHpA	C7-A	363	319	5	4.7	0.01	0.03
PFOA	C8-A	413	369	5	7.2	0.01	0.03
PFNA	C9-A	463	419	5	9.9	0.01	0.02
PFDA	C10-A	513	469	5	12.7	0.01	0.04
PFUnA	C11-A	563	519	5	15.4	0.07	0.22
PFDoA	C12-A	613	569	5	18.0	0.07	0.22
PFHxS	C6-S	399	80	55	7.9	0.01	0.03
PFOS	C8-S	499	80	55	13.8	0.01	0.04
$^{13}C_2$-PFHxA	C6-A	315	271	5	2.8	0.01	0.02
$^{13}C_4$-PFOA	C8-A	417	373	5	7.2	0.01	0.03
$^{13}C_2$-PFDA	C10-A	515	471	5	12.7	0.01	0.03
$^{13}C_4$-PFOS	C8-S	503	80	55	13.8	0.01	0.04

Note: *CE = Collision Energy
S = Perfluorinated sulfonates (PFCSs)
A = Perfluorinated carboxylic acids (PFCAs)

5.4.3 Method Recovery and Matrix Interferences

The recovery rates were calculated by spiking PFCs standards into duplicated samples. For aqueous phase samples, the standards were spiked before loading to the cartridges. While, PFCs standards were spiked into ASE cells before extraction for particulate phase analysis. The recovery rates were calculated by spiking PFCs standards into duplicated samples. Table 4.3 shows the results of recovery rates (aqueous phase) in

influent, aeration tank, effluent, and tap water samples from WWTPs and wastewater effluents from industries in different IZs (IZ1 – IZ10). Recovery rates of tap water samples were ranged from 55% – 101%; those of PFPA, PFHxA, and PFHpA were relatively low, at 55% – 81%, when comparing with other PFCs (93% – 101%). These results indicated that there were some losses during the analysis process, especially in SPE.

For industrial wastewater samples, recovery rates were ranged from 33% – 131%. In wastewater, the matrix components present in the extracted samples have potential to cause ionization suppression or enhancement of PFCs in LC/MS/MS analysis. Recovery rates of aeration tank and effluent samples were slightly lower than tap water indicating that there are some losses by the matrix effects. Furthermore, the influent samples, which have more potential of matrix interferences, showed that recovery rates were much lower than other samples by more than 20%. The recovery rates from industries effluent were in a wide range (5% – 123%) depending on types of industries. The characteristic of the wastewater from each type of industry were unique. Thus, the different matrix interferences affect the recovery rates. Development of PFCs analysis method in industrial wastewater samples was necessary to overcome the difficulty in analysis for better results. The method development for PFCs analysis will be discussed in this chapter.

5.5 Optimizing SPE Procedure for Analyzing PFCs in Environmental Water and Industrial Wastewater

5.5.1 Samples

A. *Ultrapure* water sample: samples were prepared by using *ultrapure* waters (LC/MS grade) and PFCs standards. 1 L PP bottles were used as sample containers.

B. Industrial wastewater sample: samples were collected from industrial zones (IZ2, IZ3, IZ4, IZ5, and IZ6) in 2008/6 and 2008/8. Influent, Aeration tank, and Effluent samples were collected from central wastewater treatment plant of industrial zones.

Effluents from different types of industry inside industrial zones were also collected. Samples were collected by grab-sampling using 2 L PET bottles. The samples were brought back to laboratory and did pretreatment within the same day.

5.5.2 Optimizing Options

From the difficulties in PFCs analysis as described in the last section, there are three major steps in SPE procedure that could be modified; (A) cartridge loading, (B) elution, and (C) applying matrix removal step. Analysis problems and suggested method modification are listed in Figure 5.2. Eight experiments were conducted as in Table 5.3.

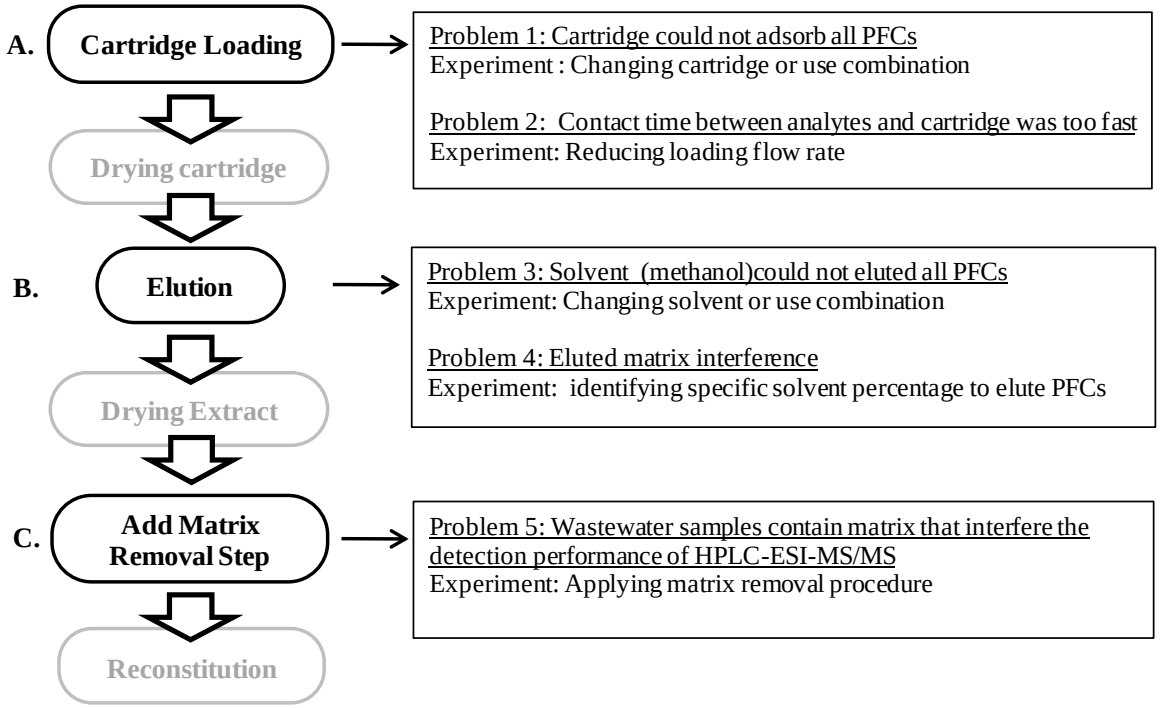


Figure 5.2 Problems and optimizing options for SPE procedure

Table 5.3 SPE modification experiments

Step	Experiment	Sample	Standard	Parameter
A. Cartridge loading	1. Single Cartridge	Ultrapure water	PFCs: 5 ng/L *(n=2)*, 10 ng/L *(n=2)*	PresepC-Agri, Oasis®HLB
	2. Combined Cartridge	Ultrapure water	PFCs: 10 ng/L *(n=4)*	PresepC-Agri + Oasis®HLB
	3. Flow rate	Ultrapure water	PFCs: 10 ng/L *(n=4)*	Flow rate 1, 5, 10 mL/min
	4. pH	Ultrapure water	PFCs: 10 ng/L *(n=1)*	pH 1, 3, 5, 7
B. Elution	5. Solvent type	Ultrapure water	PFCs: 10 ng/L *(n=4)*	methanol, acetronitrile, aceton, isopropanol
	6. Solvent %	Ultrapure water	PFCs: 10 ng/L *(n=4)*	methanol (10% - 100%), acetronitrile (10% - 100%)
	7. Solvent %	Industrial wastewater	PFCs: 10 ng/L *(n=10)*	methanol (10% - 100%), acetronitrile (10% - 100%)
C. Add Matrix Removal Method	8. Matrix Removal	Industrial wastewater	PFCs: 10 ng/L *(n=12)*	Ultrafilter, Envi-carb

5.5.3 Cartridge Selection

The first step to modify SPE process is changing cartridge which using for separate and concentrate analytes (PFCs) from the samples. PresepC-Agri (C18) was used in conventional process as described in Section 5.4. Recovery rates of PFOS and PFOA were satisfactory; however, lower recovery rates were obtained for the shorter chain PFCs. It is suggested that PFCs could not adsorb by only PresepC-Agri (C18) cartridge.

Option 1: Single cartridge comparison

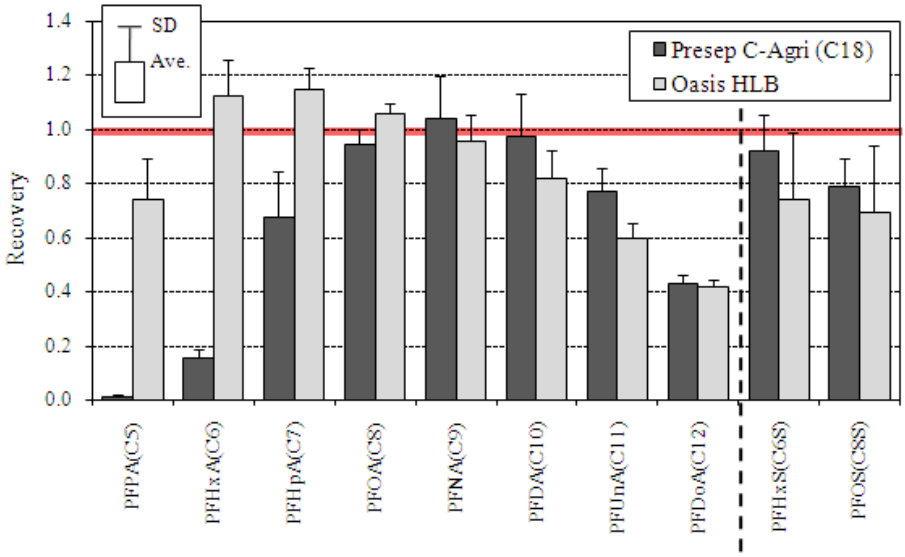


Figure 5.3 Recoveries of PresepC-Agri, and Oasis®HLB

To optimize the analytical procedure for all PFCs, two experiments (single cartridge comparison and combination of cartridges) were performed. Each experiment was done by using *ultrapure* water 1 L spiked with 5 ng/L (*n=2*) and 10 ng/L (*n=2*) PFCs standards *(total, n=4)*. Methanol (3 mL) was used as elution solvent. PresepC-Agri (C18, 6 cc, 200 mg) and Oasis®HLB (hydrophilic-lipophilic balance) Plus (6 cc, 200 mg; hereafter referred as HLB), which were commonly used in the PFCs analysis, were selected in the study (Saito *et al.*, 2003; Yamashita *et al.*, 2004; Taniyasu *et al.*, 2005). In fact, there is another cartridge that commonly use in PFCs analysis, which is Oasis®WAX. However, Oasis®WAX was not performed in this study due to the complexity of pretreatment process. As this study was mainly focused on the sampling abroad, so the simple procedure was needed.

Figure 5.3 shows analysis recoveries of PresepC-Agri and Oasis®HLB. PresepC-Agri (C18), which was used in conventional process, showed good recovery ranged from 77% - 104% for PFOA, PFNA, PFDA, PFUnA, PFHxS and PFOS, except for short-chain carboxylic acids such as PFPA, PFHxA, and PFHpA and a long-chain carboxylic acid, PFDoA. In order to improve the recovery rates of short-chain perfluorinated acids Oasis®HLB cartridge was employed. The HLB cartridges were conditioned by passage 10 mL of methanol and 10 mL *ultrapure* water, in sequence, prior to loading the samples.

The average recoveries of all PFCs for HLB were ranged from 70% - 115%, except for two long-chain carboxylates, PFUnA and PFDoA, for which the recoveries were 60% and 42%, respectively. Nevertheless, the recoveries of short-chain carboxylic acids (PFPA, PFHxA, and PFHpA) through HLB cartridges were higher than recovery rates from PresepC-Agri. In order to achieve better analytical recoveries for all PFCs analysis, the combination of PresepC-Agri and Oasis®HLB was one of the options.

To increase analysis recovery rates, the combination of PresepC-Agri with Oasis®HLB were conducted. The experiment was done by direct connecting Oasis®HLB to the outlet of PresepC-Agri (C18). The result shows that the better recovery rates were

obtained by using Oasis®HLB. Recovery rates of PFPA, PFHxA, PFHpA, PFOA and PFHxS were increased by using Oasis®HLB cartridge by 59%, 91%, 44%, 10% and 5%, respectively. Overall, the recoveries of all PFCs were above 78%, except PFPA and PFDoA, which are 60% and 44%, respectively. The low recovery of PFDoA was also found in Taniyasu *et al.*, 2005.

Option 2: Combination of cartridges

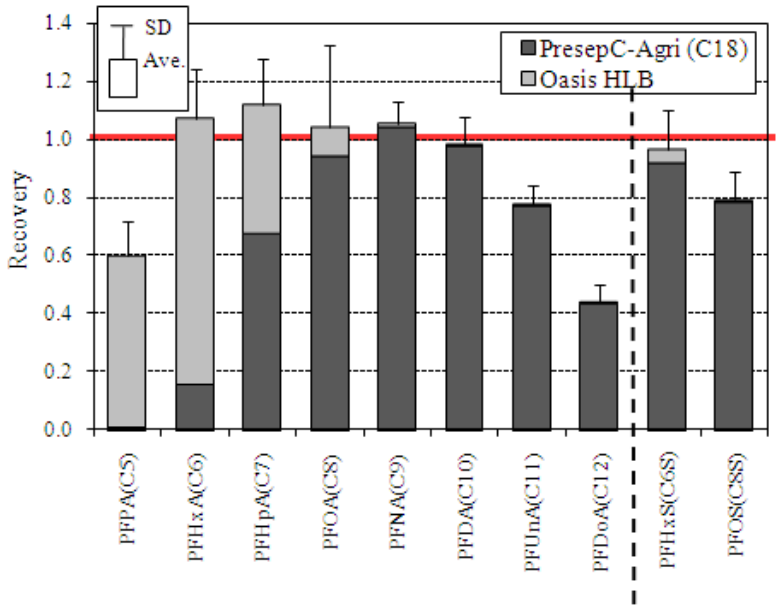


Figure 5.4 Recoveries of combination of PresepC-Agri and Oasis®HLB

5.5.4 Optimizing Flow Rate

The experiment was conducted to optimize loading flow rate that passing through the cartridges to extend contact time between PFCs and a cartridge. Flow rate 10 mL/min was used for the conventional analytical procedure. The loading flow rates of 5 and 1 mL/min were applied to samples passing through PresepC-Agri and Oasis®HLB cartridges compared to the flow rate 10 mL/min. PFCs standards 10 ng/L were spiked in the *ultrapure* water samples *(n=4)*. Methanol (3 mL) was used as elution solvent.

Figure 5.5 shows the recovery of different flow rates for cartridge loading. Flow rate 1 mL/min was low in most samples in both PresepC-Agri and Oasis®HLB cartridges. The recovery rates of PresepC-Agri with flow rate 5 mL/min were the most appropriate for

most PFCs except PFHpA, PFOA and PFNA. The recovery rates of PFCs due to different flow rates in loading Oasis®HLB cartridge were found significant differences. However, flow rate 5 mL/min were shown the most appropriate for all PFCs.

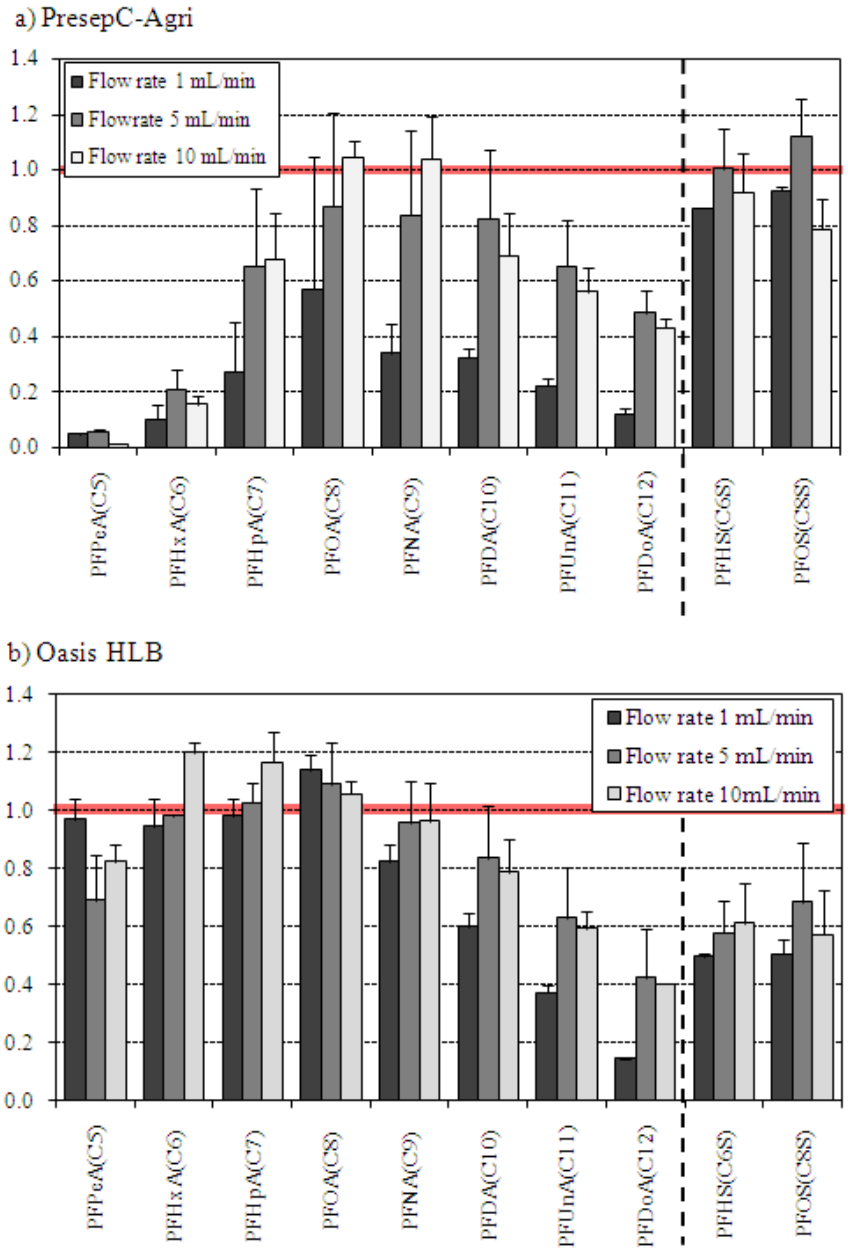


Figure 5.5 Recovery of different flow rate passed through a) PresepC-Agri and b) Oasis®HLB

5.5.5 pH variation

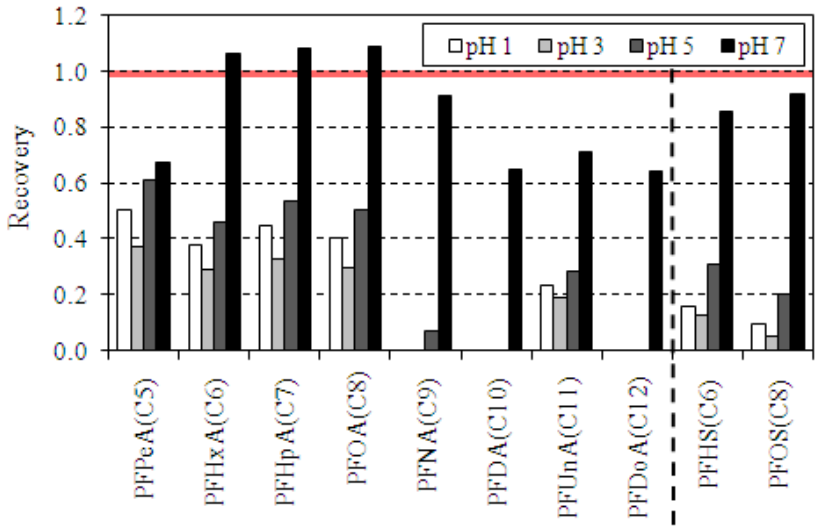


Figure 5.6 Effect of pH on the recovery through PresepC-Agri and Oasis®HLB

The effect of pH of the sample was also checked. No pH adjustment was needed in the conventional process. However, pH of industrial wastewater is in a wide range in acidic side, which can affect the performance of analysis process. The experiment was done to identify the effect of pH in the samples. Samples were prepared by *ultrapure* water spiked with 10 ng/L PFCs standards. Methanol (3 mL) was used as elution solvent. pH of the sample was adjusted to 7, 5, 3, and 1 by using 10% v/v formic acid to find the optimum pH for SPE *(n=1)*. Then, pH adjusted samples were loaded to the combined cartridge (PresepC-Agri + Oasis®HLB). Figure 5.6 shows recovery rates from pH experiment. The recovery rates of all PFCs were significant decreased by only decreased pH of the samples to 5. Therefore, pH adjustment is necessary for the lower pH samples.

5.5.6 Elution Solvent Selection

Elution experiment was performed to evaluate the suitable solvent for cartridge elution. methanol (3 mL), which was recommended by Waters Company, was used in

conventional process. Stronger strength solvents (Lough and Wainer, 1995), acetronitrile, acetone, and 2-propanol were tested in this experiment.

The experiment was done by loading PresepC-Agri (C18) and Oasis®HLB cartridges separately with spiked PFCs 10 ng/L in *ultrapure* water *(n=4)* at the flow rate 5 mL/min. Then, cartridges were dried and eluted of methanol, acetronitrile, acetone, and 2-propanol (all LC/MS grade) by 2 mL (2 times), which was recommended by Water Company. The effect of elution solvent to recovery rates was shown in Figure 5.7.

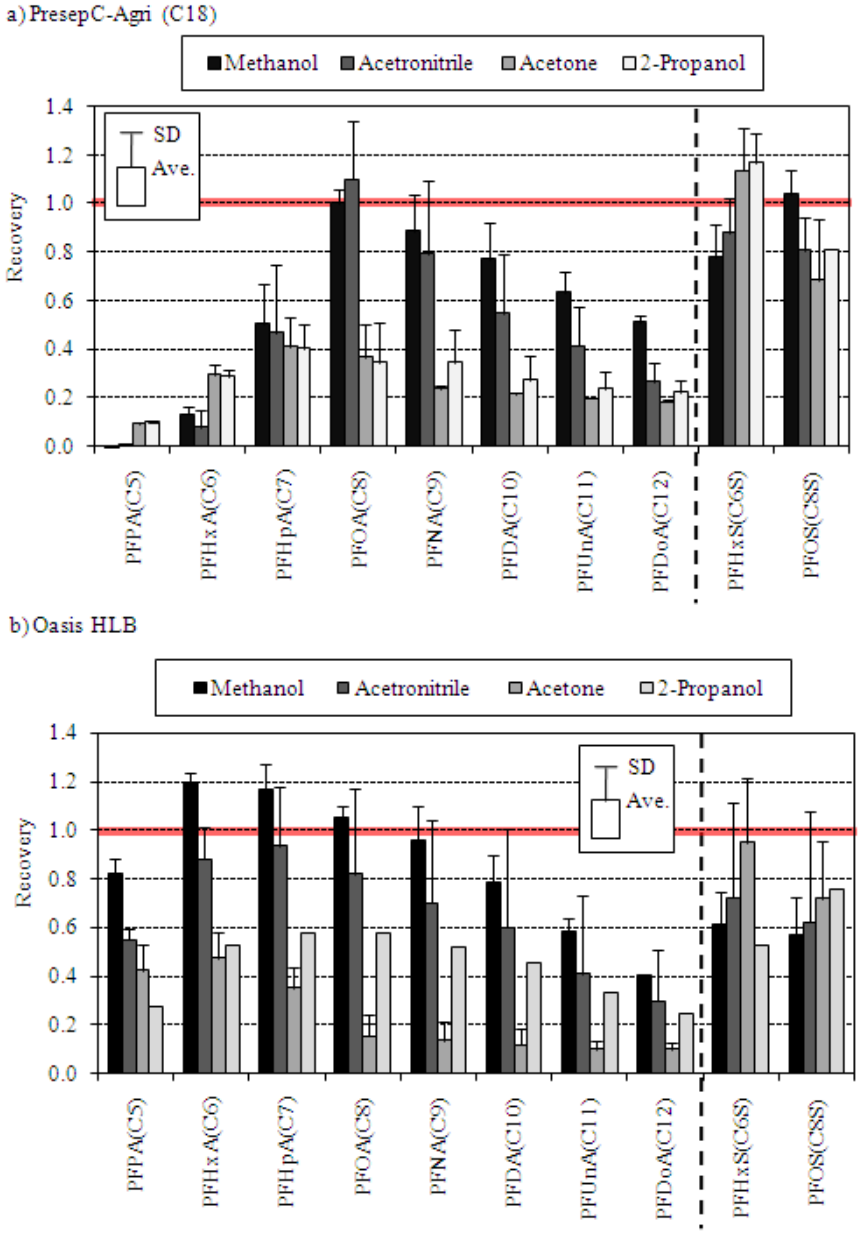


Figure 5.7 Recovery of a) PresepC-Agri and b) Oasis®HLB eluted by methanol, acetronitrile, acetone and 2-propanol

Recoveries of the samples by using methanol and acetronitrile as elution solvents were relatively higher than acetone and 2-propanol for all carboxylic acids. Methanol was the better solvent for all carboxylic acids, except PFHxA and PFHpA, which were better by eluting with acetronitrile. For perfluorinated sulfonates, recovery of acetone was better than other solvents, but acetone was not selected because recovery of acetone was very low for carboxylic acids. Acetone might suitable for research focus on perfluorinated sulfonates, but it was not suitable as a common elution solvent for all PFCs. Comparing between methanol and acetronitrile, recovery rate of acetronitrile was slightly better than methanol for eluting perfluorinated sulfonates. As a result, methanol and acetronitrile were both selected as the elution solvent. The suggested elution step was 2 mL methanol followed by 2 mL acetronitrile.

5.5.7 Methanol and Acetronitrile Percentages for Eluting PFCs

The objective of the experiment was to find suitable solvent percentages to elute each PFC. Conventional process was using 100% solvent. Matrix interferences in LC-MS/MS analysis might be decreased by changing solvent percentages. The experiment was done by loading *ultrapure* water (1 L) spiked with 10 ng/L PFCs passing through PresepC-Agri (C18), *(n*=8*)* and Oasis®HLB, *(n*=8*)* cartridges separately. The cartridges were dried after loading of samples. Half of the samples (*n*=4 for each cartridge) were eluted by varying methanol percentages (in *ultrapure* water) from 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90% and 100% (2×2 mL). Another half of the sample (*n*=4 for each cartridge) were eluted with 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90% and 100% acetronitrile (in *ultrapure* water), (2×2 mL). Totally, each cartridge was eluted ten times. The extracts were separately collected in PP tubes. The extracts were dried by N_2, reconstituted with 40% acetronitrile and analyzed by HPLC-ESI-MS/MS.

Figure 5.8 shows the percentages of PFCs eluted by different methanol percentage from PresepC-Agri and Oasis®HLB. All PFCs could elute by 80% methanol from PresepC-

Agri and 100% methanol from Oasis®HLB. The methanol percentage for elution of each PFC was varied according to hydrophobic carbon chain length (C5 ~ C12). Longer chain PFCs has higher hydrophobic value. Shorter chain PFCs such as PFPA and PFHxA were eluted by lower methanol percentage, while longer chain PFCs such as PFUnA and PFDoA eluted by higher methanol percentage. The important target compounds, PFOS and PFOA, were eluted by 60% methanol from PresepC-Agri cartridge, while PFOS and PFOA were eluted by 90% and 80% from Oasis®HLB, respectively. PFDoA, which is the most hydrophobic, was eluted by 80% methanol and 100% methanol from PresepC-Agri and Oasis®HLB, respectively.

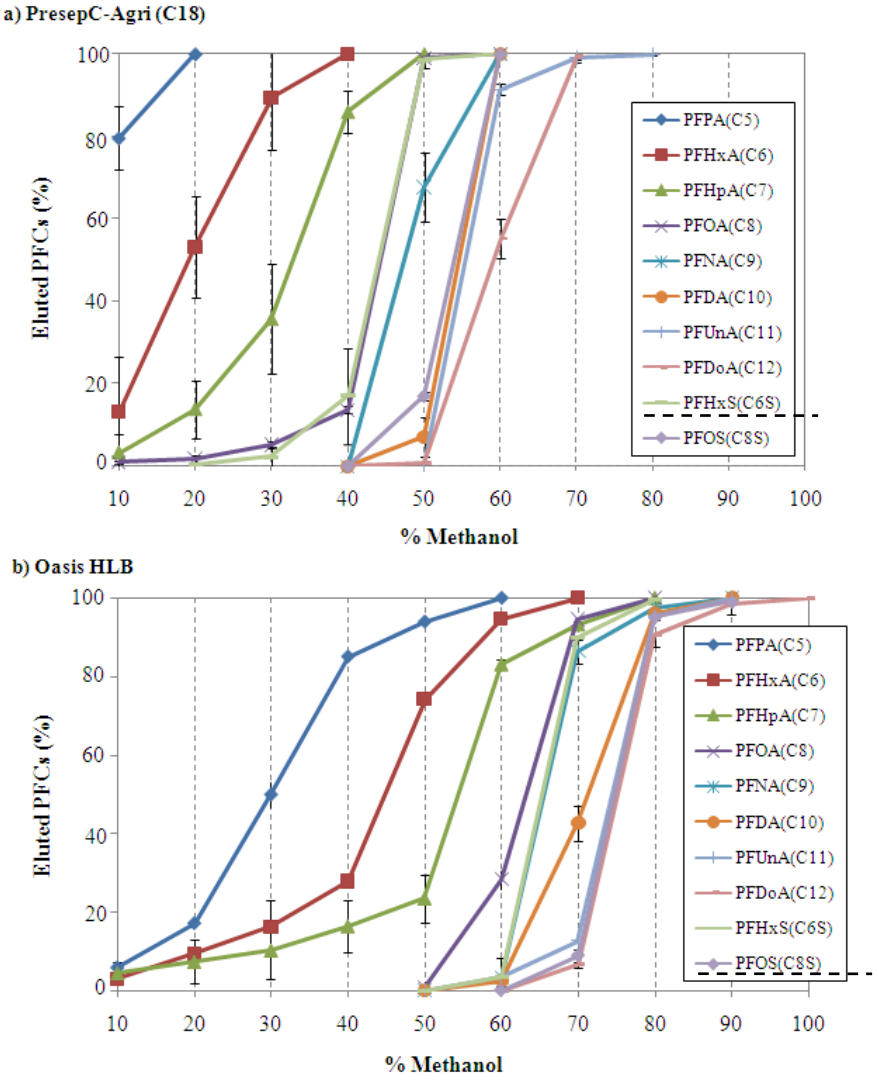


Figure 5.8 Effect of methanol percentage on recovery of PFCs in *ultrapure* water passing through PresepC-Agri (a) and Oasis®HLB (b) cartridges

Furthermore, washing step for eluting each PFC could be performed by using low methanol percentage of eluted PFCs. For example, when PFOS is only the target compound and PresepC-Agri is used as the cartridge, 40% methanol can use as washing step to eliminate other compound in the extract. In addition, this washing step can be performed together with the elution step, for instance, 40% methanol is used for washing and 60% methanol is used for elution. Thus, the specific target PFC can be eluted with less matrix interferences in the extract.

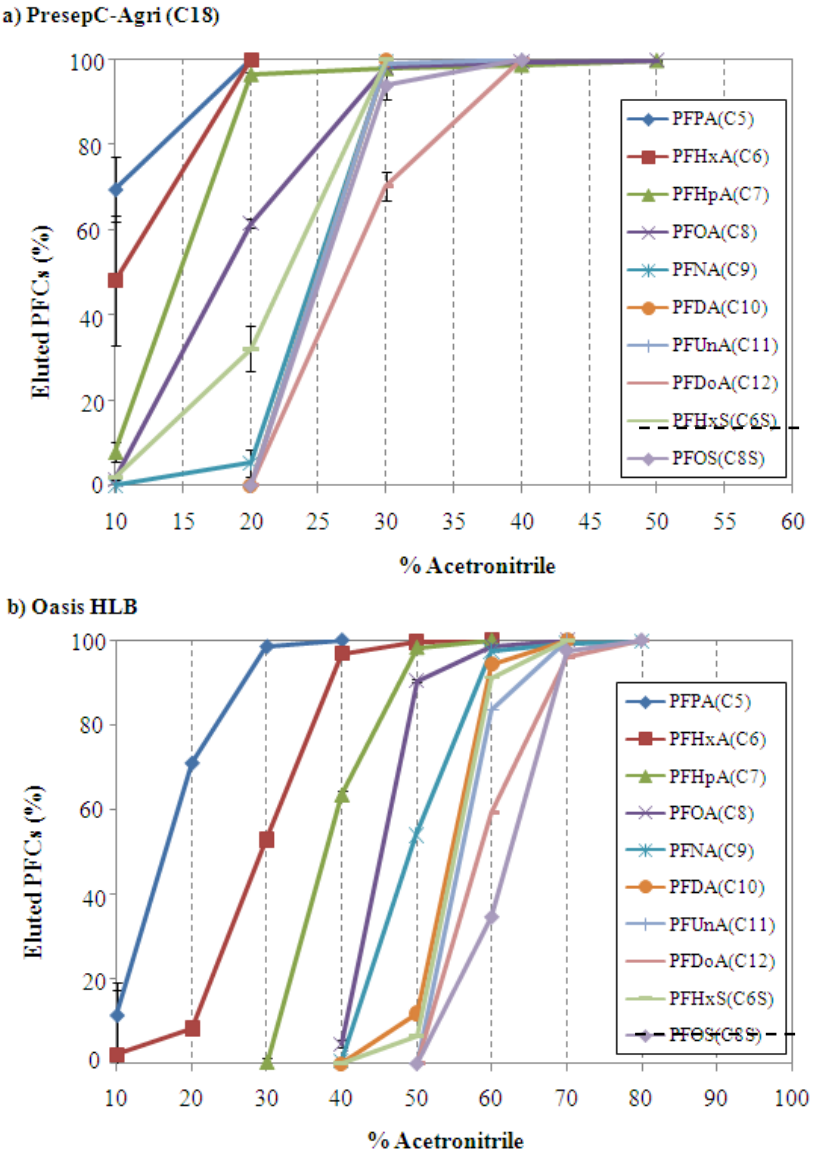


Figure 5.9 Effect of acetronitrile percentage on recovery of PFCs in *ultrapure* water passing through PresepC-Agri (a) and Oasis®HLB (b) cartridges

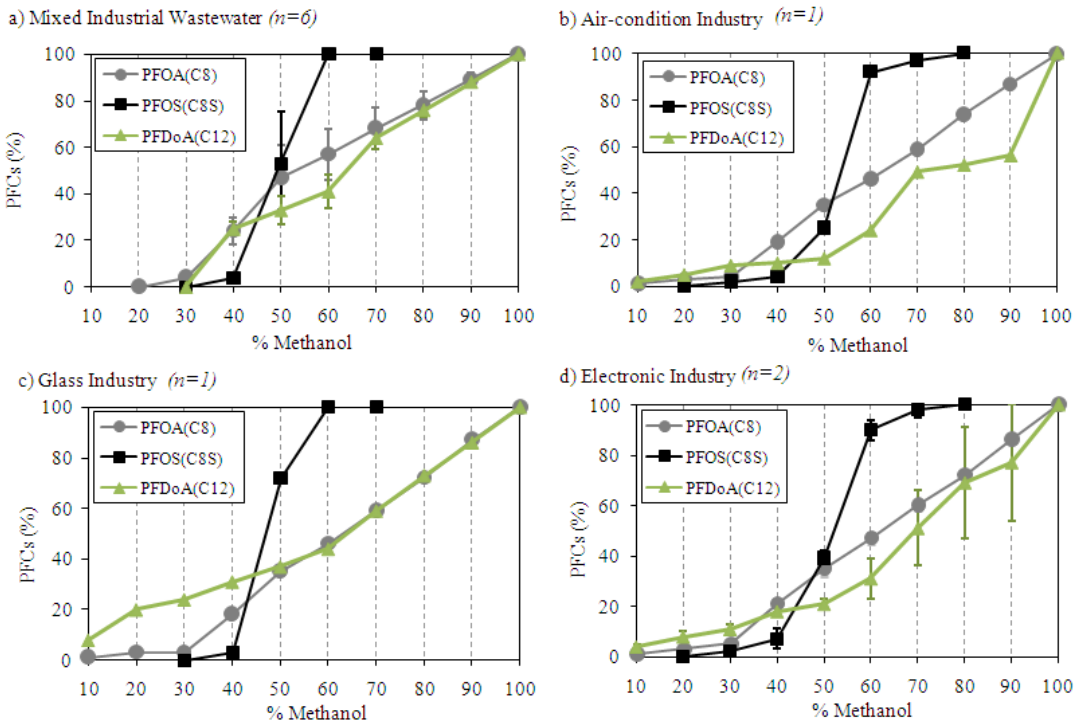
Figure 5.9 shows the percentage of PFCs eluted by different percentage of acetronitrile from PresepC-Agri and Oasis®HLB. As acetronitrile is a stronger solvent, lower percentage of solvent was needed to elute all PFCs. All PFCs could eluted by 50% acetronitrile from PresepC-Agri and 80% acetronitrile from Oasis®HLB cartridge. The action of percentage of acetronitrile on PFCs elution was similar to methanol. Weaker hydrophobic PFCs were eluted by lower solvent percentage, while stronger hydrophobic PFCs eluted by higher solvent percentage. However, the range of acetronitrile percentage to elute each PFC in PresepC-Agri was very close to each other. Hence, it is

difficult to perform a washing step. In contrast, washing step could be performed when eluting from Oasis®HLB cartridge. For example, when PFOS and PFOA were the target PFCs, washing step by 50% acetronitrile followed by 80% for elution could be performed.

5.5.8 Optimizing Elution Solvent Percentage for Industrial Wastewater Samples

Unlike the environmental water, industrial wastewater contains many chemicals and compounds that interfere the LC-MS/MS detection. Not only the matrix interference but also PFCs might attach to a bigger molecule and cannot elute with the same solvent percentages as performed in the last experiment. The similar solvent percentage experiment was performed to industrial wastewater samples to purpose the technique to reduce matrix interferences in the extracts. Samples were collected from two industrial zones. Influent, aeration tank and effluent samples were collected from industrial zones' central WWTP. Effluents from air-condition, glass and electronics industries were also collected.

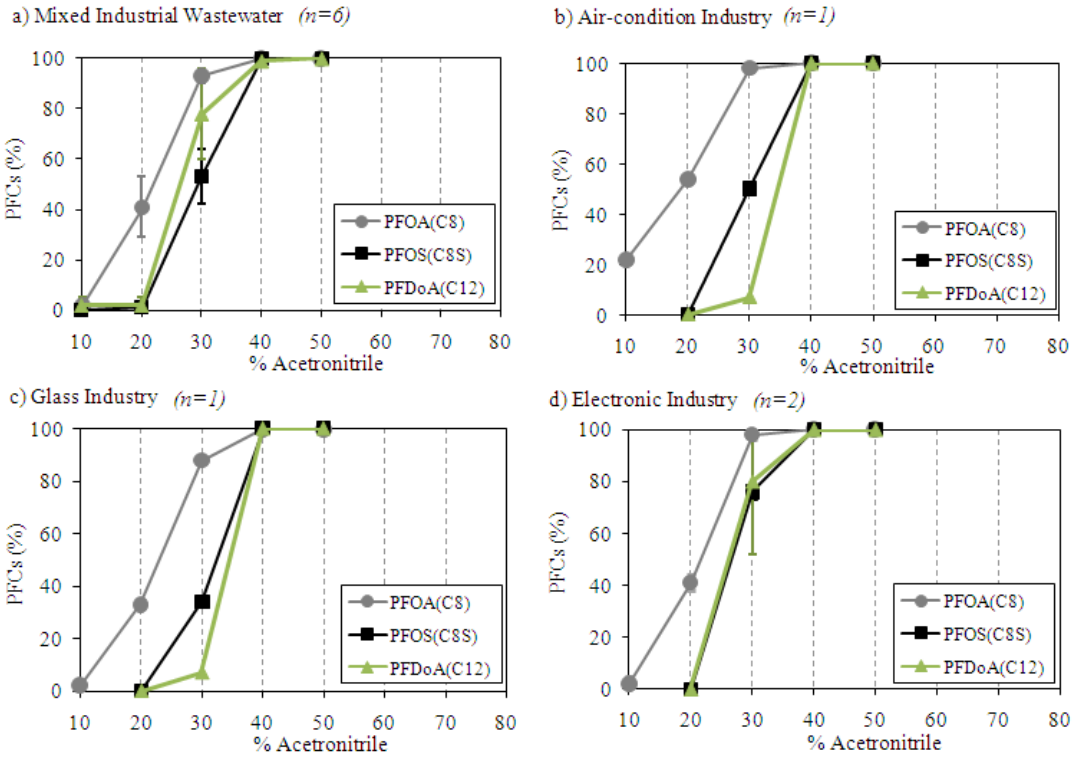
Samples were filtered with 1 µm GF/B. The filtrates (500 mL) were spiked with 10 ng/L PFCs and loading through PresepC-Agri (C18) connected with Oasis®HLB cartridges. The cartridges were dried. Samples were eluted by varying methanol percentages (in *ultrapure* water) of 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90%, and 100% (2×2 mL). Duplicated samples were eluted with 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90% and 100% acetronitrile (in *ultrapure* water), (2×2 mL). Each cartridge was eluted ten times. The extracts were separately collected in PP tubes. The extracts were dried by N_2, reconstituted with 40% acetronitrile and analyzed by HPLC-ESI-MS/MS.



Note: Mixed industrial wastewater = samples from WWTP (influent, aeration tank and effluent)

Figure 5.10 Effect of methanol percentage on recovery of PFCs in industrial wastewater samples passing through PresepC-Agri connected with Oasis®HLB

Figure 5.10 shows the result of varied methanol percentage for elution from a) mixed industrial wastewater, b) air-condition industry, c) glass industry and d) electronics industry. Only PFOS, PFOA, and PFDoA were shown in the graph because the strongest solvent was used to elute PFDoA, which has the strongest hydrophobic property . The result was different from *ultrapure* water experiment. All of PFOS could elute by 70 – 80% methanol, which is similar to *ultrapure* water experiment. While, 100% methanol was required for eluting PFOA and other carboxylic acids. The reason might be the perfluorinated acids can easily attached to the matrix and needed higher solvent strength to elute. Significant difference of percentage for elution were not shown in all types of wastewater. .



Note: Mixed industrial wastewater = samples from WWTP (influent, aeration tank and effluent)

Figure 5.11 Effect of acetronitrile percentage on recovery of PFCs in industrial wastewater samples passing through PresepC-Agri connected with Oasis®HLB

Figure 5.11 shows the effect of acetronitrile on recovery of PFCs in industrial wastewater samples passing through PresepC-Agri connected with Oasis®HLB. For acetronitrile, all PFCs could be eluted by 50% acetronitrile in all samples. Results were not shown much difference in all types of samples. Hence, 50% acetronitrile could be used for all PFCs elution to reduce the matrix interference in industrial wastewater samples.

5.5.9 Matrix Removal Procedure

After elution of the samples, matrixes were still present in the extract. Matrix removal procedure was necessary to increase the recovery of industrial wastewater samples. Samples were collected from two industrial zones, IZ (A) and IZ (B). Influent, aeration tank and effluent samples were collected from industrial zones' central WWTP.

Effluents from air-condition, plastic and electronics industries were also collected. Two matrix removal methods, Supelclean Envi-Carb cartridge and Ultrafilter (Molecular weight cut off = 10,000) were applied to remove matrixes, which interfere during analysis in LC/MS/MS.

Figure 5.12 Matrix removal procedures a) Supelclean Envi-Carb b) Ultrafilter

Supelclean Envi-Carb was purchased from Sigma-aldrich Company. The cartridge was previously used to remove the matrix in soil and sediment samples in another study (Powley *et al.*, 2005). The experiment was performed by connected Supelclean Envi-Carb directly to the cartridges when performed elution process (Figure 5.12). The matrixes were trapped in the Envi-Carb, while PFCs were passed through. Another method for matrix removal was using ultrafilter (purchased from Advantech Company), which can filter molecules larger than 10,000 Mw. All of the molecules of PFCs were smaller than the ultrafilter (<1,000 Mw). Ultrafilter was applied after eluted samples were dried and reconstituted with 1 mL methanol (LC/MS grade), (Figure 5.12). The extract was passed through ultrafilter and then the filter was rinsed by 2 mL methanol.

Total 3 mL methanol was dried under N_2 and reconstituted with 40% acetronitrile for LC/MS analysis.

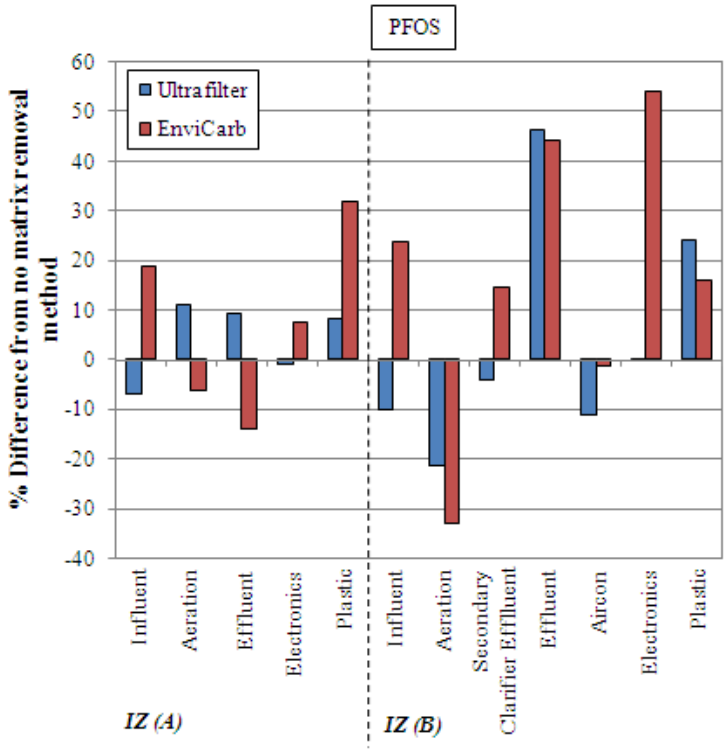


Figure 5.13 Percentage (%) of recovery increased when using matrix removal for PFOS

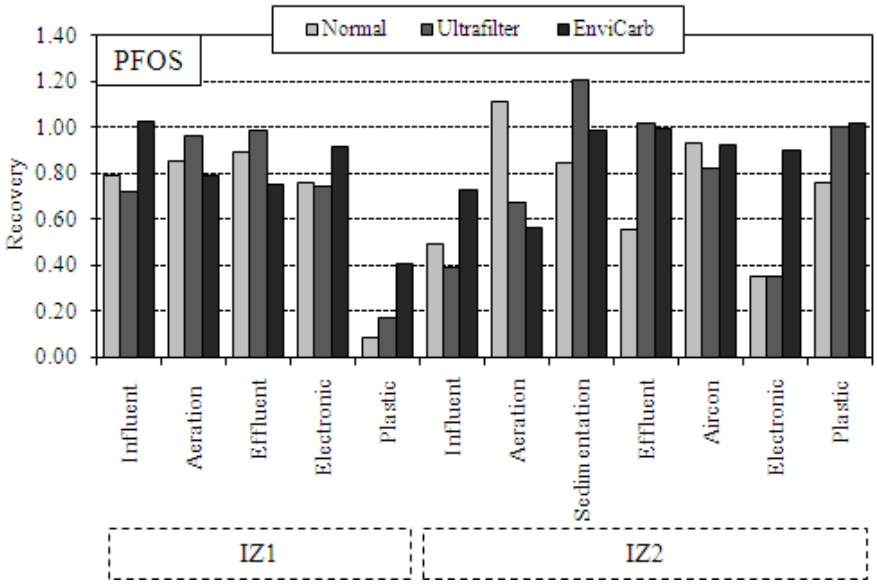


Figure 5.14 Recoveries of industrial wastewater samples by applying matrix removal procedure for PFOS analysis

Figure 5.13 shows the percentage improvement when using matrix removal methods for PFOS. Ten out of twelve samples were shown the increasing of recovery when using either Ultrafilter or Envi-Carb. Envi-Carb was effective to remove the matrix that affects the PFOS detection in the effluent samples of electronics and plastic industries from both industrial zones. The recoveries increased by average of 31% and 24% for analyzing samples from electronics and plastic industries, respectively. Ultrafilter was also effective for the effluents from plastic company with the average improvement 16%. Both cartridges were not good for the effluent of the air condition industry. The variation of the recoveries in analyzing of WWTP samples was occurred. This might come from the complexity of wastewater, which was the mixing of different types of effluent from the industries. However, Envi-Carb was shown effective to remove matrix in the influent of WWTP, while Ultrafilter was better to apply for effluent samples. Figure 5.14 shows the recoveries of the samples.

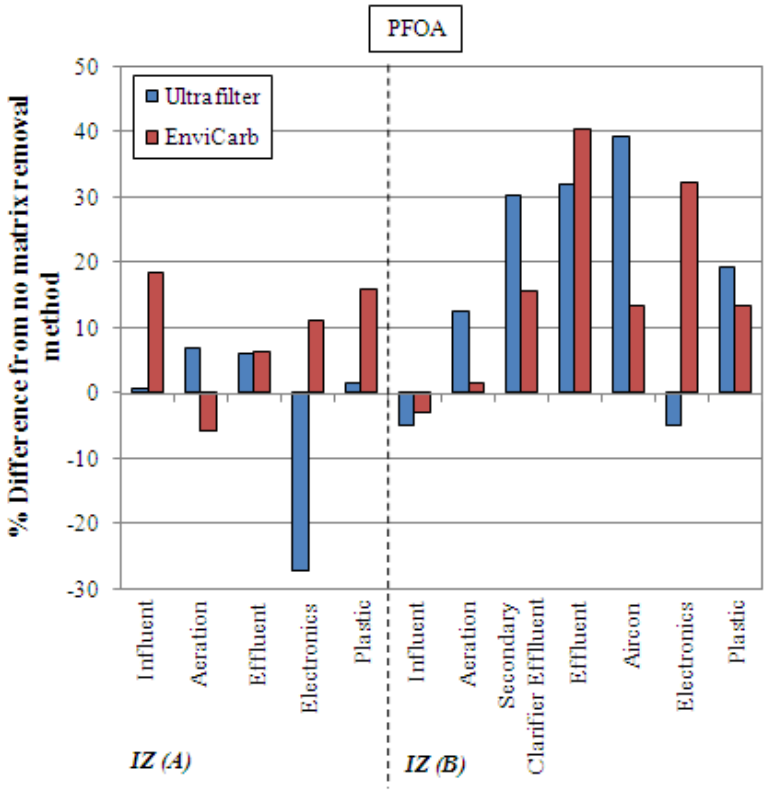


Figure 5.15 Percentage (%) of recovery increased when using matrix removal method for PFOA

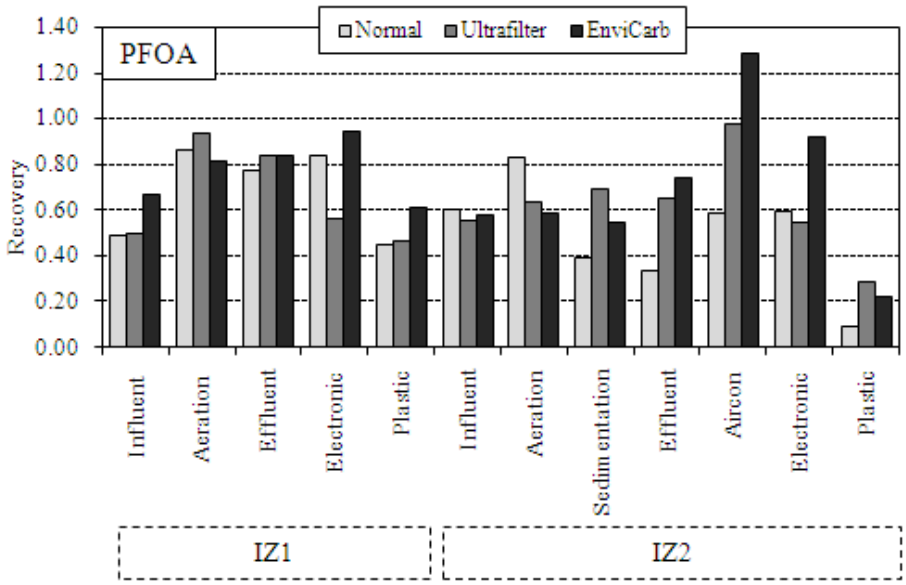


Figure 5.16 Recoveries of industrial wastewater samples by applying matrix removal procedure for PFOS analysis

Figure 5.15 shows the percentage improvement when using matrix removal methods for PFOA. Recoveries of most samples were improved by using matrix removal method, except influent sample in IZ (B). Envi-Carb was effective for effluent samples from electronics and plastic industries, which is similar to PFOS. The recoveries were increased by 22% and 15% for analyzing PFOA in electronics and plastic industrial samples, when using Envi-Carb as the matrix removal method. Ultrafilter was not good for analyzing effluents from electronics industries. However, both two matrix removal method was good for air-condition industrial sample. Recovery by using Ultrafilter was increased 39%. Moreover, Ultrafilter was the effect ways to remove the matrix in mixed industrial wastewater samples. The recoveries were increased in most samples in WWTP especially in aeration tank and effluent samples. Figure 5.16 shows the recoveries of the samples.

5.6 Summary

Several options were applied to overcome the analytical problems in analyzing water and wastewater samples by optimizing SPE procedure. Recoveries of PresepC-Agri and

Oasis®HLB were identified. The combination of these two cartridges was the better option for analyzing PFCs in water samples. The optimum flow rate for loading the samples was 5 mL/min for both cartridges. Methanol (2 mL) plus Acetronitrile (2 mL) was the effective way to elute PFCs from the cartridges. The specific solvent percentages to elute each PFCs were identified for both water and industrial wastewater samples. The matrix removal methods by using Envi-Carb and Ultrafilter were effective to remove the matrix in different types of industrial wastewater samples. The summarized of the method for analyzing water and industrial wastewater samples were shown in Table 5.4.

Table 5.4 Summary of analysis method for water and industrial wastewater samples

Target Compound	Type of sample	Cartridge	Elution solvent	Solvent % (methanol, acetronitrile)	Matrix Removal
PFOS/PFOA	Tap water	PresepC-Agri (C18)	2 mL methanol + 2 mL acetronitrile	80%, 50%	None
	Surface water	PresepC-Agri (C18)		80%, 50%	None
Ten PFCs	Tap water	PresepC-Agri (C18) & OasisHLB		100%, 100%	None
	Surface water			100%, 100%	None
	Industrial wastewater				
	WWTP			100%, 50%	Ultrafilter
	Electronic			100%, 50%	Envi-Carb
	Plastic			100%, 50%	Ultrafilter or Envi-Carb
	Air-condition			100%, 50%	Ultrafilter

Chapter 6

Perfluorinated Compounds Contamination in Tap Water and Drinking Water in Bangkok, Thailand

6.1 Introduction

PFOS and PFOA have been found not only in the environment but also in wildlife and human blood (Hansen *et al*., 2001; Kannan *et al*., 2004). The toxicity of PFOS has been studied for many years. At laboratory testing, PFOS has been shown to be toxic in rats and rabbits. The lowest observed adverse effect level (LOAEL) was 0.4 mg/kg bw/day and no observed adverse effect level (NOAEL) of PFOS was estimated to be 0.1 mg/kg bw/day (OECD, 2002). Nevertheless, a PFOS risk assessment to human still to date has not been verified.

PFCs problems in tap and drinking water could be a great concern. Researchers have reported PFCs contamination in raw water (river), tap, and drinking water in Japan (Saito *et al*., 2004; Takagi *et al*., 2008), the USA (Boulanger *et al*., 2004; Hansen *et al*., 2002), and Europe (Ericson *et al*., 2008; Skutlarek *et al*., 2006). Unfortunately, the study on PFCs contamination in tap and drinking water is very limited in South East Asian countries, especially in Thailand. A comprehensive survey of PFCs in tap water and drinking water in the country is necessary for better understanding on the risk exposure of PFCs to human. In the mean time, evaluation of the conventional water treatment process is also important for understanding the behavior and removal of PFCs during the processes.

6.2 Objectives

The purposes of this study were to identify the occurrence of PFCs in tap water and drinking water in Bangkok city, to evaluate the conventional water treatment processes

performance on the removal of PFCs, and to compare PFCs contaminations with other Asian cities.

6.3 Materials and Methods

6.3.1 Sampling Location

There are four water treatment plants (WTP), (W1-W4), in the Bangkok city providing tap water for more than eight million people. The source of water for W1, W2, and W3 is the Chao Phraya River. The pumping station is located in Pathum Thani province, north of Bangkok. Raw water is pumped to "East Water Canal" and flows to W1 and W2. There is a pumping station in the canal to transfer raw water to W3 across Chao Phraya River. W4 is located in the west side of Bangkok, taking raw water from Mae Klong River, which is located 107 km west from W4. "West Water Canal" was built to transfer raw water from Mae Klong River to W4. The conventional process is used in all four treatment plants as shown in Figure 6.1.

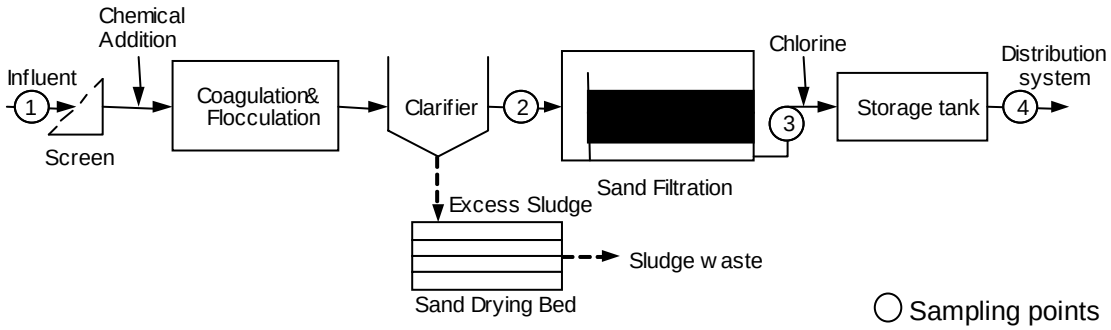
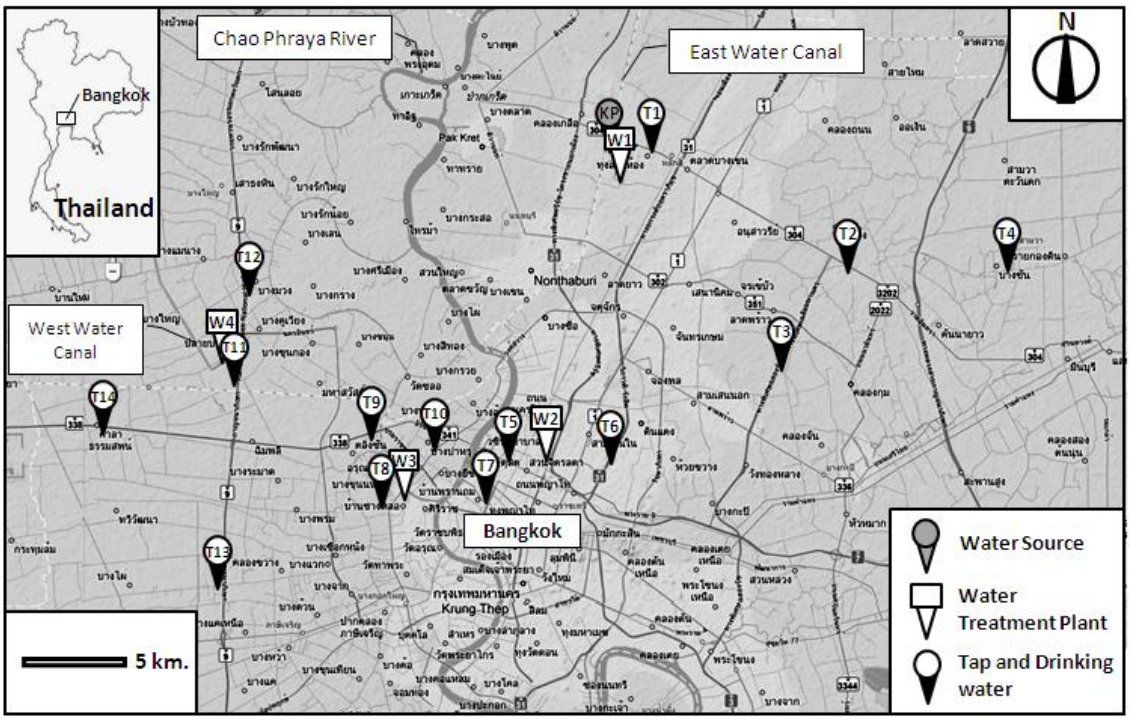


Figure 6.1 Sampling points in WTPs

The sampling was conducted in all four WTPs in January, 2009. Raw water, clarifier effluents, rapid sand filter effluents, and tap water samples were collected in each WTP to identify the performance of treatment processes. Tap water samples (T1-T14) from each treatment plant were also collected from gas stations around Bangkok to estimate PFCs contamination in tap water. Tap water sampling was conducted on the same day of each WTP sampling. Ten bottles of drinking water of five commercial companies,

whose raw water have different origins, were also purchased from nearby convenient stores. Sampling points are shown in Figure 6.2.



Source: Google Maps

Figure 6.2 Sampling locations for raw water, WTPs, tap, and drinking water samples

6.3.2 Sample Collection

WTP and tap water samples were collected by direct grab-sampling from the faucet. Bottled drinking water samples were purchased in 2 L PET bottles from convenient stores. New 1.5 L narrow-neck PET bottles with screw caps were used as sampling containers. PET bottles were washed using methanol and dried before use. Containers were also rinsed three times with sample before collection. After sampling, the samples were brought back to laboratory, stored in the refrigerator at 4ºC, and sample pre-treatment was carried out immediately after returning from sampling.

6.3.3 Sample Preparation

Collected samples were directly loaded into the cartridge except influent and primary sedimentation tank's effluent in WTP samples, which needed suspended solid filtration by using 1 µm GF/B glass fiber filter. The fiber filter was then further analyzed by using Accelerated Solvent Extraction (ASE-200) from Dionex, Japan. The aqueous phase sample (1000 mL) was passed through a PresepC-Agri (C18) cartridge (Wako, Japan) inline connected to Oasis®HLB (Waters, Japan), which were preconditioned by 10 mL of LC/MS-grade methanol followed by 20 mL *Milli-Q* water manually. PFCs mass labeled surrogates ($^{13}C_2$-PFHxA, $^{13}C_4$-PFOA, $^{13}C_2$-PFDA, and $^{13}C_4$-PFOS) were spiked (10 ng/L) into a sample before loading to find their recovery rate. A flow rate of 5 mL/min was maintained through the cartridge. The above procedures were completed in Thailand and the cartridges were brought back to Japan for further analysis. In Japan, each cartridge was dried completely under vacuum. Then, the target compounds were eluted with 2 mL LC/MS-grade methanol followed by 2 mL LC/MS grade acetronitrile into a polypropylene tube, evaporated to dryness with nitrogen gas, and reconstituted into LC/MS mobile phase (40% LC/MS-grade acetronitrile) to a final volume of 2 mL. PFCs in filtrates were concentrated by a factor of 500 times.

The suspended solids phase was separated by GF/B filter (Filtered volume: 1000 mL). The filters were air dried and inserted to ASE cells (Volume: 33 mL) for extraction. The surrogates were spiked into the duplicated cell before extraction. The extraction was done by using Methanol as a solvent. The extraction was run three cycles (15 min per one cycle) by using pressure 2000 psi and temperature 100ºC. Final extracted volume was 60 – 80 mL. Then, the extracted sample was diluted with LC/MS-grade *ultrapure* water into 1 L, loaded to the cartridges, and continued with the same procedure as liquid phase samples. A duplicated sample was performed for each sampling point.

6.3.4 Instrumental Analysis and Quantification

Separation of PFCs was performed by using Agilent 1200 SL high-performance liquid chromatography (HPLC), (Agilent, Japan). Extract of 10µL was injected to a 2.1×100

mm (5 µm) Agilent Eclipse XDB-C_{18} column. Mobile phase consisted of (A) 5mM ammonium acetate in *ultrapure* water (LC/MS grade) and (B) 100% Acetronitrile (LC/MS grade). At a flow rate of 0.25 mL/min, the separation process started with initial condition of 30% (B), increased to 50% (B) at 16.5 min, then to 70% (B) at 16.6, held at 70% (B) for 3.4 min, went up to 90% (B) at 21 min, kept at 90% (B) for 1 min, and then ramped down to 30% (B). The total running time was 34 min for each sample. For quantitative determination, the HPLC was interfaced with an Agilent 6400 Triple Quadrupole (Agilent, Japan) mass spectrometer (MS/MS). Mass spectrometer was operated with the electro spray ionization (ESI) negative mode. Analyte ions were monitored by using multiple reactions monitoring (MRM) mode. The analytical parameters of each PFC are shown in Table 6.1.

Table 6.1 Analytical parameters of each PFC by HPLC/MS/MS analysis

Compound	No. of Carbon	Parent ion (*m/z*)	Daughter ion (*m/z*)	CE* (eV)	Retention time (min.)	LOD (ng/L)	LOQ (ng/L)
PFPA	C5-A	263	219	5	1.9	0.02	0.05
PFHxA	C6-A	313	269	5	2.8	0.01	0.02
PFHpA	C7-A	363	319	5	4.7	0.01	0.03
PFOA	C8-A	413	369	5	7.2	0.01	0.03
PFNA	C9-A	463	419	5	9.9	0.01	0.02
PFDA	C10-A	513	469	5	12.7	0.01	0.04
PFUnA	C11-A	563	519	5	15.4	0.07	0.22
PFDoA	C12-A	613	569	5	18.0	0.07	0.22
PFHxS	C6-S	399	80	55	7.9	0.01	0.03
PFOS	C8-S	499	80	55	13.8	0.01	0.04
$^{13}C_2$-PFHxA	C6-A	315	271	5	2.8	0.01	0.02
$^{13}C_4$-PFOA	C8-A	417	373	5	7.2	0.01	0.03
$^{13}C_2$-PFDA	C10-A	515	471	5	12.7	0.01	0.03
$^{13}C_4$-PFOS	C8-S	503	80	55	13.8	0.01	0.04

Note: *CE = Collision Energy
S = Perfluorinated sulfonates (PFCSs)
A = Perfluorinated carboxylic acids (PFCAs)

6.3.5 Calibration and Validation

The calibration curves for quantification, consisting of seven points covering 0.05 to 25 µg/L (0.2 to 100 ng/L with concentrated factor), generally provided linearity with

determination coefficients (R^2) more than 0.999 in every compound. Limit of detection (*LOD*) for HPLC/MS/MS was defined as concentration with signal to noise ratio (*S/N*) equal to 3:1. Practically, *LOQ* was used for quantifying analytes, which was defined by *S/N* 10:1 (Saito *et al*., 2004; Lien, 2007) (Table 6.1). The duplicated analysis was also performed on all samples and coefficients of variations (*CV*) of concentrations were below 20%. During the sample collection and analysis, analytical blanks were performed by using *ultrapure* water. PFCs concentrations were less than the *LOQ*, indicating no contamination during the process.

The recovery rates were calculated by spiking PFCs surrogates into samples. For aqueous phase samples, surrogates were spiked before loading to the cartridges, while, the standards were spiked into ASE cells before extraction for particulate phase analysis. The ranges (average) of recovery rates of $^{13}C_2$-PFHxA, $^{13}C_4$-PFOA, $^{13}C_2$-PFDA, and $^{13}C_4$-PFOS were 61 – 136% (95%), 79 – 125% (105%), 74 – 124% (101%), and 73 – 126% (98%), respectively.

6.4 Occurrences of PFCs in Water Treatment Plant, Tap water, and Drinking water

6.4.1 PFCs Concentrations

The concentration of ten PFCs in raw water, WTPs, tap water, and drinking water samples are summarized in Table 6.2. PFCs were detected in all tap water and drinking water samples, revealing that they contaminate mostly tap and drinking water in the city. PFPA, PFHxA, PFHpA, PFOA, and PFOS were detected in most samples, while other five PFCs (PFNA, PFDA, PFUnA, PFDoA, and PFHxS) were not detected (*ND*) or lower than the limit of quantification (<*LOQ*). PFCs concentration ranges in the samples were 0.28 – 2.88 ng/L for PFPA, *ND* – 0.43 ng/L for PFHxA, *ND* – 1.65 ng/L for PFHpA, 1.43 – 16.54 ng/L for PFOA, and 0.22 – 6.28 ng/L for PFOS. The average combined ten PFCs in the samples ranged from 3.31 to 25.79 ng/L.

PFOS and PFOA concentrations in raw water (originated from Chao Phraya River) were at 4.29 ng/L and 16.54 ng/L, respectively. These values were comparable to the previous reported PFCs concentrations in Chao Phraya River, which ranged from 0.19 – 2.20 ng/L PFOS and 1.1 – 20.4 ng/L PFOA (Lien, 2007). The highest concentration of PFCs was detected in raw water with concentrations of 25.79 ng/L. While, average combined concentration of ten PFCs in effluent was at 3.63 ng/L, indicating that there was some removal of PFCs by conventional water treatment processes. The detailed discussions on PFCs removal are discussed later in this chapter.

Table 6.2 PFCs concentration in raw water, water treatment plant (WTP), tap water, and drinking water samples

Type of sample		*n*	PFCs concentrations (ng/L)									
			PFPA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFDoA	PFHxS	PFOS
Raw water		2	2.88±0.08	0.43±0.01	1.65±0.04	16.54±2.10	ND	ND	<LOQ	ND	ND	4.29±0.19
WTP:	Influent	8	2.23±1.53	0.17±0.04	0.68±0.29	9.57±2.41	ND	ND	<LOQ	ND	ND	5.02±3.32
	Clarifier	8	1.14±0.62	0.15±0.15	0.70±0.33	9.08±2.67	ND	ND	<LOQ	ND	ND	6.28±3.58
	Rapid sand filter	8	1.20±0.48	ND	ND	1.43±1.26	ND	ND	<LOQ	ND	ND	0.68±0.33
	Effluent	8	1.11±0.71	ND	ND	1.79±2.13	ND	ND	<LOQ	ND	ND	0.73±0.43
Tap water		28	1.84±1.72	0.13±0.07	0.28±0.14	3.60±4.15	ND	ND	<LOQ	ND	ND	0.18±0.27
Drinking water		20	0.28±0.34	0.34±0.30	0.25±0.18	10.55±9.58	ND	ND	ND	ND	ND	0.22±0.37

Note: *n* = Number of samples, A = Perfluorinated carboxylic acids (PFCAs), S = Perfluorinated sulfonates (PFCSs),
ND = Not Detected , <LOQ = Lower than Limit of Quantification

Tap water was collected from 14 sampling points around Bangkok city. The average combined concentrations of ten PFCs were found at 6.03 ng/L. The concentration was much higher comparing to WTP's effluent samples (finally treated tap water) (3.63 ng/L). Although the reason for higher concentrations of PFCs in tap water was not well understood, it might be possible that PFCs contamination occurred in the water distribution system such as pipe leakage, which is a normal case of water losses in Bangkok city (MWA, 2008).

In this survey, five brands of bottled drinking water samples were purchased from tap water sampling locations in Bangkok. The sources of bottled drinking water originated from different places, not only in Bangkok. Advanced treatment processes such as

Reverse Osmosis membrane, Ozonation, and UV disinfection were normally used for bottled drinking water. Even after using advanced treatment processes, PFCs were still detected in all samples. Average PFCs concentrations in bottled drinking water ranged from 0.22 to 10.55 ng/L, PFOA is the highest among other PFCs. Comparing with tap water, PFCs were found at a much higher concentration in bottled drinking water. It appears that the advanced treatment processes was not effective to remove PFCs in the real scale application. The result in our study was similar to the early report from Osaka, Japan (Tagaki *et al*., 2008).

6.4.2 Relative Abundance of PFCs

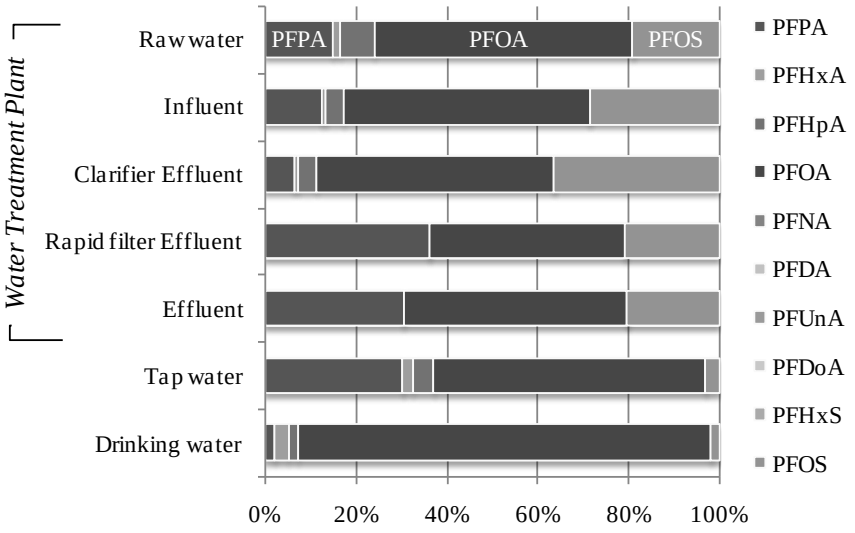


Figure 6.3 Relative abundances of PFCs in raw water, water treatment plant, tap water, and drinking water samples

Figure 6.3 shows the relative abundance of PFCs in different samples. The concentrations of PFCs in the raw water and WTP samples followed the general trends of PFOA > PFOS > PFPA. PFOA (57%), PFOS (19%), and PFPA (15%) were the dominant PFCs in raw water. PFHxA and PFHpA were detected in lower percentage with 8% and 2%, respectively, while other PFCs were not detected in all the samples. The relative abundance of PFCs in influent and clarifier effluent samples also showed similar relation. The rapid sand filter effluent and WTP effluent samples showed a different proportion with PFOA > PFPA > PFOS, while PFHxA and PFHpA were not

detected. The results showed that rapid sand filter have some effects on PFCs removal. PFOA was the dominant PFC in tap water (60%) and drinking water (90%). The highest PFOA among other PFCs in tap and drinking water samples were also shown in the results of Ericson *et al*. (2008).

6.4.3 PFOS and PFOA Contaminations in Tap Water

Sampling was conducted in Bangkok city where fourteen sampling points were selected. There consisted of four tap water sampling points in each W1 and W4 area, which produced total tap water of 4.4 million m^3/d. Three tap water samples were collected in each W2 and W3 area, which are the smaller WTPs producing total of 870,000 m^3/d. Table 6.3 shows PFOS and PFOA concentrations and loadings in tap water. The average PFOS and PFOA concentrations in tap water were detected at 0.17 and 3.58 ng/L, respectively.

Table 6.3 PFOS and PFOA concentrations in tap water

Water Treatment Plant	Flow rate (m^3/d)	Sample	Concentration (ng/L)	
			PFOS	PFOA
W1	3,600,000	T1	0.56±0.06	1.62±0.09
		T2	0.25±0.32	0.55±0.11
		T3	0.25±0.15	0.80±0.21
		T4	0.24±0.15	0.80±0.27
		Ave	**0.33**	**0.94**
W2	700,000	T5	*ND*	0.72±0.13
		T6	0.06±0.09	0.82±0.13
		T7	0.45±0.04	1.36±0.29
		Ave	**0.17**	**0.97**
W3	170,000	T8	*ND*	1.43±0.57
		T9	*ND*	10.37±0.53
		T10	0.11±0.16	5.71±1.42
		Ave	**0.04**	**5.84**
W4	800,000	T11	*ND*	1.04±0.19
		T12	*ND*	9.00±4.20
		T13	0.04±0.06	6.03±0.10
		T14	0.56±0.79	10.15±8.16
		Ave	**0.15**	**6.56**

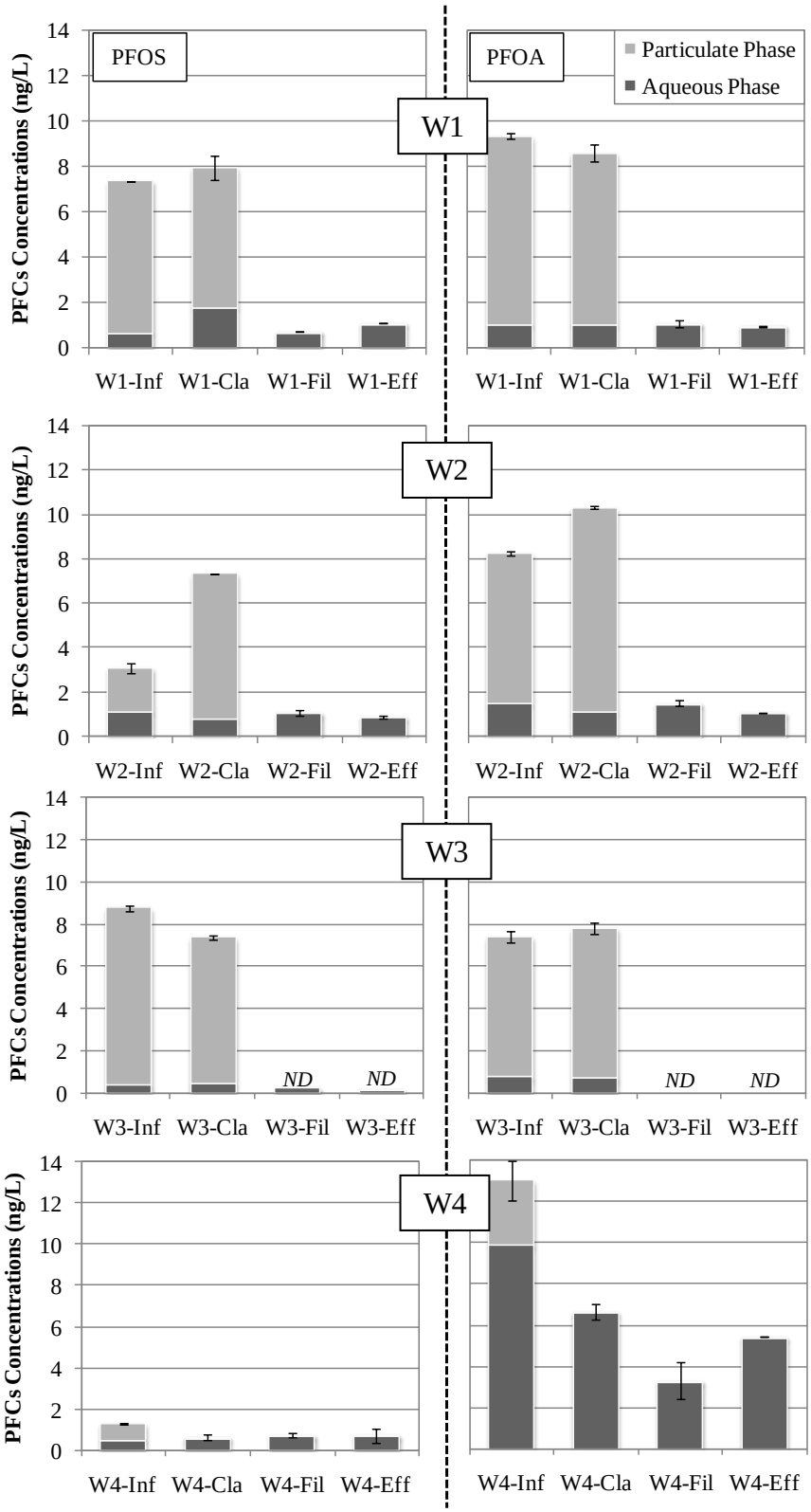
Note: *ND* = not detected, Ave = average

The concentration of PFOS decreased when compared to Lien, 2007, which reported that the average PFOS in tap water in Bangkok city was at 5.29 ng/L in 2006, while PFOA concentration was comparable (4.19 ng/L). The recent studies have shown declining concentration of PFOS in tap water, environmental, and blood samples following the phase-out of PFOS production (Tagaki *et al*., 2008; Renner, 2008).

W1 and W2 are located in the east side of Bangkok distributing tap water to 82% of the population in the city. The average PFOS concentrations distributed from W1 and W2 were at 0.33 and 0.17 ng/L, respectively. PFOA concentration in tap water samples were recorded at 0.94 ng/L from W1 and 0.97 ng/L from W2. The total loading of 1.31 mg/d PFOS and 4.06 mg/d PFOA were daily distributed from W1 and W2, respectively. For the western Bangkok, W3 and W4 produced 970,000 m^3/d of tap water to 18% of Bangkok population. PFOS and PFOA were found to be at 0.04 ng/L and 5.84 ng/L respectively in tap water samples from W3. Higher concentrations were identified at W4, which produces tap water covering for 82% of western area, with a level of 0.15 ng/L of PFOS and 6.56 ng/L of PFOA. Daily PFOS and PFOA loadings were at 0.13 mg/d and 6.24 mg/d, respectively. The result shows that PFOS and PFOA were not evenly distributed in all areas in the city. In this case, PFOA was detected higher in the western area, while PFOS concentration was quite similar in all areas. PFOS and PFOA concentrations were based on many factors such as source of water, treatment processes, etc. This comprehensive study of PFOS and PFOA concentration in the city is valuable for the further study of risk assessment in the city. Currently, there is no standard of guideline value of PFOS and PFOA in Thailand. However, based on the value reported by New Jersey Department of Environmental Protection (2009), PFOA concentrations in tap water found in Bangkok is not expected to cause any health risks.

6.4.4 Water Treatment Plant Processes Performance

The aqueous phase and particulate phase concentrations of PFOS and PFOA in different samples in four WTPs are illustrated in Figure 6.4. PFOS and PFOA were detected in particulate phase in most samples (influent and clarifier effluent samples). W1, W2, and W3 have same water source. PFOS and PFOA concentrations were detected much higher in particulate phase than liquid phase having ratio of 9.5:1.



Note: Inf = Influent of WTP, Cla = Effluent of Primary Clarifier, Fil = Effluent of Rapid Sand Filtratrion, Eff = Effluent of WTP

Figure 6.4 PFOS and PFOA concentrations in four WTPs

In contrast, W4, which has different raw water source, had much lower particulate: liquid ratio with 0.94:1 indicating that this ratio was depending on the sources of the water. It seemed that PFOS and PFOA in particulate phase were effectively removed by rapid sand filtration in W1, W2, and W3, while, PFOS and PFOA in W4 were effectively removed by the primary sedimentation.

For the liquid phase samples, PFOS and PFOA concentrations were quite similar during the treatment processes in most WTPs except PFOA in W3 and W4. The removal rate of PFOA in W3 and W4 were at 100% and 45%, respectively. However, the average removal rates of PFOS and PFOA in aqueous phase were recorded at 45% and -4%, respectively. These removal rates were comparable to the earlier report of Takagi *et al*. (2008), which supports the breakdown of precursors to PFOS and PFOA during the treatment processes. Although some percentages of PFOS can be removed by the current treatment processes, the removal rates of PFCs were lower than 50% in most WTPs.

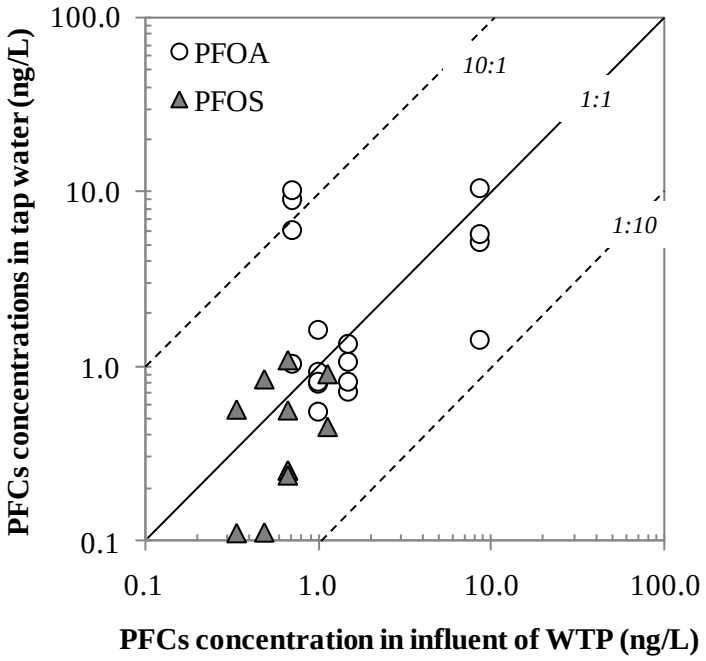


Figure 6.5 Relationship between PFOS and PFOA concentrations in aqueous phase of influent of WTP and tap water

Figure 6.5 shows the relationship between PFOS and PFOA concentrations in aqueous phase of influent of WTP and tap water. 80% of PFOS plots and 88% of PFOA plots varied around linear line 1:1; representing that the treatment process did not completely remove PFCs. There was a limitation on removal of PFCs in aqueous phase samples. In general, it can be concluded that the current treatment process was not able to remove PFCs completely. Nevertheless, PFCs in particulate phase were effectively removed by the rapid sand filtration.

6.4.5 Comparing PFOS and PFOA Concentrations among Other Asian Cities

Previous studies have reported PFOS and PFOA concentrations in tap water and drinking water from Asian cities including Kuala Lumpur, Singapore, Hanoi, Shenzhen, Taipei, Osaka, and Tokyo (Tanaka *et al.*, 2008; Takagi *et al*., 2008; Lien, 2007). Figure 6.6 shows PFOS and PFOA concentrations in Bangkok and other Asian cities. PFOS concentrations varied from 0.18 to 7.34 ng/L. Bangkok tap water and drinking water samples had lower average PFOS concentration among the detected, while the highest was detected in Taipei. PFOS detected in tap water in the South East Asian cities (Bangkok, Kuala Lumpur, Singapore, and Hanoi) were lower than Shenzhen, Taipei, Osaka, and Tokyo.

The trends of PFOS concentrations were comparable to those in surface waters (Figure 3.11), which are the sources of tap water. PFOA concentrations ranged from 2.50 to 14.75 ng/L. Detected PFOA in Bangkok city was the highest among the other cities in South East Asian. Average PFOA concentration in tap water in Bangkok city was comparable to Shenzhen but much lower than Osaka and Tokyo, which was the same level as PFOA detected in drinking water in this study. However, the highest PFOA detected was in tap and drinking water samples which did not exceed the guideline of New Jersey Department of Environmental Protection (2009).

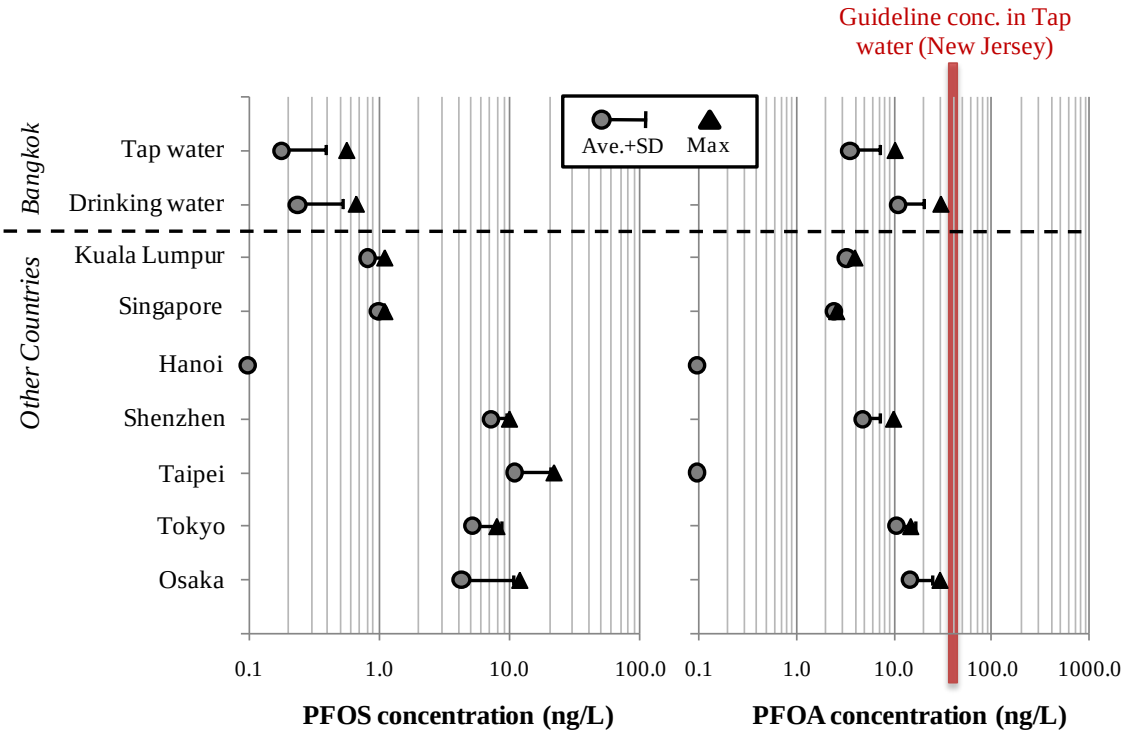


Figure 6.6 Comparison of PFOS and PFOA concentrations with other Asian cities

6.5 Summary

PFCs were detected in all tap water and drinking water samples. PFPA, PFHxA, PFHpA, PFOA, and PFOS were detected in most samples, while other five PFCs (PFNA, PFDA, PFUnA, PFDoA, and PFHxS) were not detected (*ND*) or lower than the limit of quantification (<*LOQ*). The concentrations of PFCs in the raw water and WTP samples followed the general trends of PFOA > PFOS > PFPA. PFOS and PFOA concentrations in raw water were found to be at 4.29 ng/L and 16.54 ng/L, respectively. The average PFOS and PFOA concentrations in tap water were detected at 0.17 and 3.58 ng/L, respectively. Comparing with tap water, PFCs were found to be of much higher concentration in bottled drinking water. The tap water results also showed that PFOS and PFOA were not similarly distributed to all area in the city. In this case, PFOA were detected higher in the western area, while PFOS concentration was quite similar in all areas.

The average removal rates of PFOS and PFOA in aqueous phases were 45% and -4%, respectively. In general, it can be concluded that the current water treatment processes do not completely remove PFCs. Nevertheless, PFCs in particulate phase were effectively removed by the primary sedimentation and rapid sand filtration. Currently, there is no standard of guideline value of PFOS and PFOA in Thailand. However, based on the value reported by New Jersey Department of Environmental Protection (2009), PFOA concentrations in tap water and drinking water found in Bangkok was not expected to cause any health risks.

Chapter 7

Mass Flow Analysis of Perfluorinated Compounds in Industrial Wastewater Treatment Plants

7.1 Introduction

PFCs are used in the consumer products and are found in municipal wastewater (Boulanger *et al*., 2005; Schultz *et al*., 2006) and sludge (Higgins *et al*., 2005). Wastewater Treatment Plants (WWTPs) were considered as one possible source of releasing PFCs. As PFCs are widely applied in industrial production process, industrial WWTPs could be a major point source of PFCs releasing to water environment. PFCs have many applications in industries such as surfactants, surface treatment, fire retardants, and coating materials. Some researchers have already reported that their major sources seemed to be related to industrial activities (Taniyasu *et al*., 2005; Hansen *et al*., 2002; Lien, 2007). In Chapter 4, the occurrences of PFCs from the industrial activities were identified. IZ2 and IZ5 were the major industrial zones releasing these chemicals. PFCs were detected in all samples, including industries effluents and samples in WWTPs. However, the distribution and fate of PFCs during industrial wastewater process, specifically for both aqueous and particulate phases, are not recognized. This chapter will focus on the PFCs mass flows in the industrial zones.

7.2 Objectives

The purposes of this study were to identify PFCs concentrations from central WWTP inside industrial zones, to identify PFCs mass flow in central WWTP in industrial zones, and to determine industrial wastewater treatment processes performance on removal of PFCs.

7.3 Materials and Methods

7.3.1 Sampling Locations

Two industrial WWTPs (IZ2 and IZ5) were selected for this mass flow study (Figure 4.1). Many types of industries were located in the area including electronics, chemical, paper, plastic, glass, etc., that have potential of releasing PFCs. There are 316 factories in IZ2 and 484 factories in IZ5. All industries discharge their wastewater into central WWTP of each IZ. Central WWTP in IZ2 has daily wastewater intake capacity of 12,000 m^3/d and it operates with conventional activated sludge (AS) process (Figure 7.1). Samples were collected from influent, aeration tank, secondary clarifier effluent, effluent and sludge.

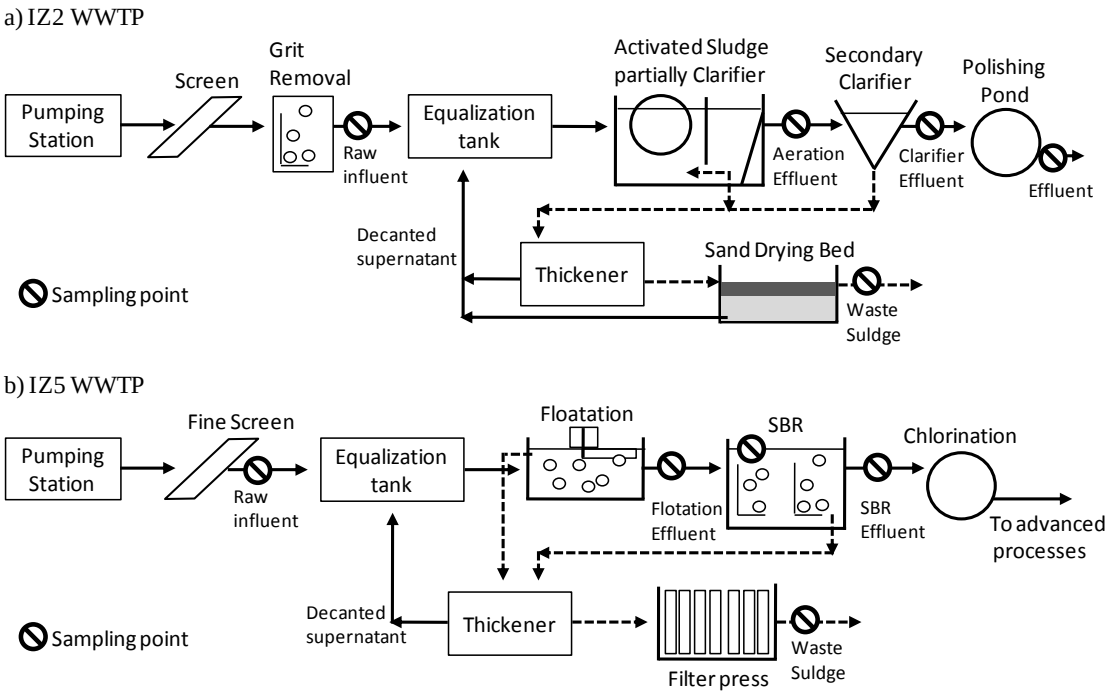


Figure 7.1 Schematic of the industrial wastewater treatment plants

WWTP in IZ5 has daily wastewater intake capacity of 20,000 m^3/d, and Sequencing Batch Reactor (SBR) system coupled with advanced treatment system were used in this treatment plant. However, this chapter will focuses only on biological processes.

Samples were collected from SBR system including influent, floatation effluent, aeration tank, sedimentation effluent, and sludge from aeration tank.

7.3.2 Sample Collection

Samples were collected from different processes (influent, aeration tank, secondary clarifier effluent, effluent and sludge) every two hour at 9:00, 11:00, 13:00, 15:00, and 17:00 on 2009/1/20 for IZ2 and on 2009/1/22 for IZ5. Samples were collected by grab-sampling using a polypropylene container. New 1.5 L narrow-neck PET bottles with screw caps were used as sampling containers. PET bottles were washed by methanol and dried prior to use. PET bottles and sampling containers were also rinsed three times with sample before collection. Wastewater samples were refrigerated at 4ºC in laboratory and pretreatments steps (in Thailand) were completed within 48 hrs after arriving sampling.

7.3.3 Sample Preparation

A collected sample was filtered by 1 µm GF/B glass fiber filter to separate suspended solids. The filter was then further analyzed by using Accelerated Solvent Extraction (ASE-200) from Dionex, Japan. The aqueous phase sample (500 mL) was passed through a PresepC-Agri (C18) cartridge (Wako, Japan) inline connected to Oasis®HLB (Waters, Japan), which were preconditioned by 10 mL of LC/MS-grade methanol followed by 20 mL *ultrapure* water manually. PFCs mass labeled internal standards ($^{13}C_2$-PFHxA, $^{13}C_4$-PFOA, $^{13}C_2$-PFDA, and $^{13}C_4$-PFOS) were spiked (10 ng/L) into a sample before loading to find their recoveries. A flow rate of 5 mL/min was maintained through the cartridge. The above procedures were completed in Thailand and the cartridges were brought back to Japan for further analysis. In Japan, each cartridge was dried completely under vacuum. Then, the target compounds were eluted with 2 mL LC/MS-grade methanol followed by 2 mL 50% acetronitrile:*ultrapure* water into a polypropylene tube, evaporated to dryness with nitrogen gas and reconstituted with 1 mL LC/MS-grade methanol. The extract was filter with Ultrafilter to remove the matrixes. Ultrafiilter was rinsed with 1×1 mL LC/MS-grade methanol. The extract was

evaporated with N_2 and reconstituted into LC/MS mobile phase (40% LC/MS-grade acetronitrile) to a final volume 2 mL. PFCs in filtrates were concentrated by a factor of 250 times.

The suspended solids phase was separated by GF/B filter (Filtered volume: 500 mL). The filters were air dried and inserted to ASE cells (Volume: 33 mL) for extraction. The internal standards were spiked into the duplicated cell before extraction. The extraction was done by using methanol as a solvent. The extraction was run three cycles (15 min per one cycle) by using pressure 2000 psi and temperature 100ºC. Final extracted volume was 60 – 80 mL. Then, the extracted sample was diluted with LC/MS-grade ultrapure water into 1 L, loaded to the cartridges, and continued with the same procedure as liquid phase samples. The duplicated sample was performed for each sample.

7.3.4 Instrumental Analysis and Quantification

Separation of PFCs was performed by using Agilent 1200SL high-performance liquid chromatography (HPLC), (Agilent, Japan). Extract 10µL was injected to a 2.1×100 mm (5 µm) Agilent Eclipse XDB-C_{18} column. Mobile phase consisted of (A) 5mM ammonium acetate in *ultrapure* water (LC/MS grade) and (B) 100% Acetronitrile (LC/MS grade). At a flow rate of 0.25 mL/min, the separation process started with initial condition of 30% (B), increased to 50% (B) at 16.5 min, then to 70% (B) at 16.6, held at 70% (B) for 3.4 min, went up to 90% (B) at 21 min, kept at 90% (B) for 1 min, and then ramped down to 30% (B). The total running time was 34 min for each sample. For quantitative determination, the HPLC was interfaced with an Agilent 6400 Triple Quadrupole (Agilent, Japan) mass spectrometer (MS/MS). Mass spectrometer was operated with the electrospray ionization (ESI) negative mode. Analyte ion monitored by using multiple reaction monitoring (MRM) mode. The analytical parameters of each PFC are shown in Table 7.1.

Table 7.1 Analytical parameters of each PFC by HPLC/MS/MS analysis

Compound	No. of Carbon	Parent ion (*m/z*)	Daughter ion (*m/z*)	CE* (eV)	Retention time (min.)	LOD (ng/L)	LOQ (ng/L)
PFPA	C5-A	263	219	5	1.9	0.02	0.05
PFHxA	C6-A	313	269	5	2.8	0.01	0.02
PFHpA	C7-A	363	319	5	4.7	0.01	0.03
PFOA	C8-A	413	369	5	7.2	0.01	0.03
PFNA	C9-A	463	419	5	9.9	0.01	0.02
PFDA	C10-A	513	469	5	12.7	0.01	0.04
PFUnA	C11-A	563	519	5	15.4	0.07	0.22
PFDoA	C12-A	613	569	5	18.0	0.07	0.22
PFHxS	C6-S	399	80	55	7.9	0.01	0.03
PFOS	C8-S	499	80	55	13.8	0.01	0.04
$^{13}C_2$-PFHxA	C6-A	315	271	5	2.8	0.01	0.02
$^{13}C_4$-PFOA	C8-A	417	373	5	7.2	0.01	0.03
$^{13}C_2$-PFDA	C10-A	515	471	5	12.7	0.01	0.03
$^{13}C_4$-PFOS	C8-S	503	80	55	13.8	0.01	0.04

Note: *CE = Collision Energy
S = Perfluorinated sulfonates (PFCSs)
A = Perfluorinated carboxylic acids (PFCAs)

7.3.5 Calibration and Validation

The calibration curves for quantification, consisting of seven points covering 0.05 to 25 µg/L (0.2 to 100 ng/L with concentrated factor), generally provided linearity with determination coefficients (R^2) more than 0.999 in every compound. *LOQ* was used for quantifying analyte, which was defined by *S/N* 10:1 (Saito *et al*., 2004; Lien, 2007) (Table 7.1). The duplicated analysis was also performed on all samples and coefficients of variations (*CV*) of concentrations were below 20%.

The recovery rates were calculated by spiking PFCs internal standards into samples. For aqueous phase samples, internal standards were spiked before loading to the cartridges, while, the standards were spiked into ASE cells before extraction for particulate phase analysis. The recovery rates of $^{13}C_2$-PFHxA, $^{13}C_4$-PFOA, $^{13}C_2$-PFDA, and $^{13}C_4$-PFOS were ranged 61-131%, 63-121%, 84-145%, and 60-112%, respectively.

7.3.6 Calculation of Mass Flow

The average mass flow of each PFC was determined by multiplying the average PFC concentration by system flow rate. The actual flow rates on the sampling day were 8,400 m^3/d in IZ2 and 16,080 m^3/d in IZ5. Mass flow of the sludge was calculated by multiplying sludge concentration, specific gravity, and sludge discharge volume per day. The sludge discharges per day from IZ2 and IZ5 were 220 and 480 m^3/d, respectively. The specific gravity was calculated from the following equation (Metcalf & Eddy *et al*., 2003).

$$\frac{Ws}{S_s \rho_w} = \frac{W_f}{S_f \rho_w} + \frac{W_v}{S_v \rho_w}$$

where; Ws = weight of solid

S_s = specific gravity of solids

ρ_w = density of water

W_f = weight of fixed solids

S_f = specific gravity of fixed solid

W_v = weight of volatile solids

S_v = specific gravity of volatile solid

Solid content of sludge is 5%. Ratio of fixed solids to volatile solids equal to 4:1 (IZ2) and 2:1 (IZ5), which were calculated from solids fractions in activated sludge process. The specific gravity of fixed solids and volatile solids were 2.5 and 1.0, respectively. Then, the specific gravity of solid in IZ2 was as follows;

$$\frac{1}{S_s} = \frac{0.8}{2.5} + \frac{0.2}{1} = 0.52$$

$S_s = 1.92$ (IZ2)

$S_s = 1.67$ (IZ5)

The specific gravity of the sludge (include water) of IZ2 was as follows;

$$\frac{1}{S_s} = \frac{0.05}{1.92} + \frac{0.95}{1} = 0.98$$

$S_s = 1.03$ (IZ2)

$S_s = 1.02$ (IZ5)

7.4 PFCs in Solid and Liquid Phase

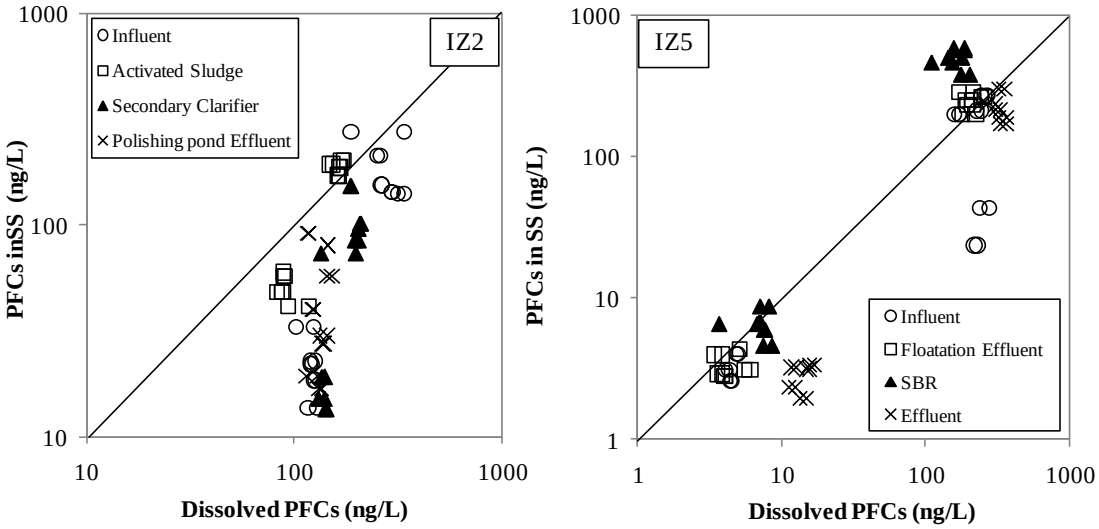


Figure 7.2 Relationship of PFCs concentrations in liquid and solid phases in IZ2 and IZ5 WWTPs

PFCs analysis was done in both dissolved and suspended solids in wastewater samples. Figure 7.2 shows the relationship of PFCs concentrations in liquid and solid phases in different samples of IZ2 and IZ5 WWTP. Most of the plots in IZ2 were below linear line 1:1, indicating that the PFCs concentration in dissolved phase was higher than PFCs in SS. Higher PFCs in SS were detected only in activated sludge and some influent samples. In IZ5, most of the plots were varied near the linear line 1:1. Similar to IZ2, higher PFCs concentrations in SS were contained in activated sludge process. Furthermore, all effluent samples contained higher PFCs level in dissolved phase due to most of the solid fraction removed by secondary clarifier.

7.5 PFCs Concentrations

Survey was conducted in WWTP in selected industrial zones. PFCs were detected in both wastewater and sludge in most samples, except PFDoA in effluent and sludge samples in IZ5. Average PFCs concentrations in IZ2 and IZ5 WWTPs were shown in Table 7.2. Total PFCs concentrations in wastewater samples in IZ2 were 847 ng/L in influent and 662 ng/L in effluent in IZ2. Sludge samples from WWTPs contained 1,539 ng/g of total PFCs. PFOS, PFOA, PFDA, and PFHpA were the dominant PFCs accounting for 42%, 19%, 15%, and 11% (Figure 7.3), respectively, while the other PFCs were less than 10%. PFOS concentration in effluent (190 ng/L) was comparable to our last survey (183 ng/L) in 2008/8. PFOA concentration also showed similar result 149 ng/L (this survey) and 158 ng/L in 2008/8.

Table 7.2 Average PFCs concentrations in IZ2 and IZ5 WWTPs

Sample		PFCs concentration (ng/L)									
		PFPA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFDoA	PFHxS	PFOS
IZ2	Influent	14.4	70.0	32.2	142.1	15.3	63.1	3.1	10.0	31.7	465.4
	Activated Sludge	29.4	79.4	43.3	142.0	12.1	81.3	11.9	48.4	26.8	348.7
	Secandary Clarifier Effluent	26.2	84.9	43.5	149.8	21.4	81.4	3.8	7.6	28.8	296.2
	Polishing pond Effluent	32.4	77.4	46.8	149.8	24.0	118.8	5.8	7.9	8.7	190.1
	Sludge (ng/g)	2.9	99.9	52.6	136.0	10.2	327.7	45.2	310.6	157.7	396.9
IZ5	Influent	0.5	0.1	0.8	6.6	174.5	1.5	81.9	1.2	25.8	381.3
	Floatation Effluent	1.1	0.4	1.0	7.9	207.9	1.2	136.7	1.4	24.4	460.8
	Activated Sludge (SBR)	7.6	0.5	1.7	13.7	308.4	4.8	338.2	7.6	27.5	672.9
	Effluent	7.9	1.0	1.8	16.9	353.2	1.8	157.6	ND	50.4	552.8
	Sludge (ng/g)	6.7	0.6	1.6	11.3	512.8	7.5	78.2	ND	48.8	736.7

In IZ5, total PFCs concentration in influent and effluent were 674 ng/L and 1,143 ng/L, respectively. Total PFCs concentration in the sludge was 1,404 ng/g. PFOS and PFOA concentrations in the effluent in this survey were lower than the last survey in 2008/8, which were 1,357 ng/L and 28 ng/L, respectively. Different from IZ2, PFOS, PFNA, and PFUnA were the dominant PFCs in IZ5 accounting for 51%, 26%, and 18% (Figure 7.3), respectively. It is indicated that each industrial zone had the specific PFCs profile because different types of industry discharged different wastes. The similar relative abundances of PFCs was detected in all wastewater samples.

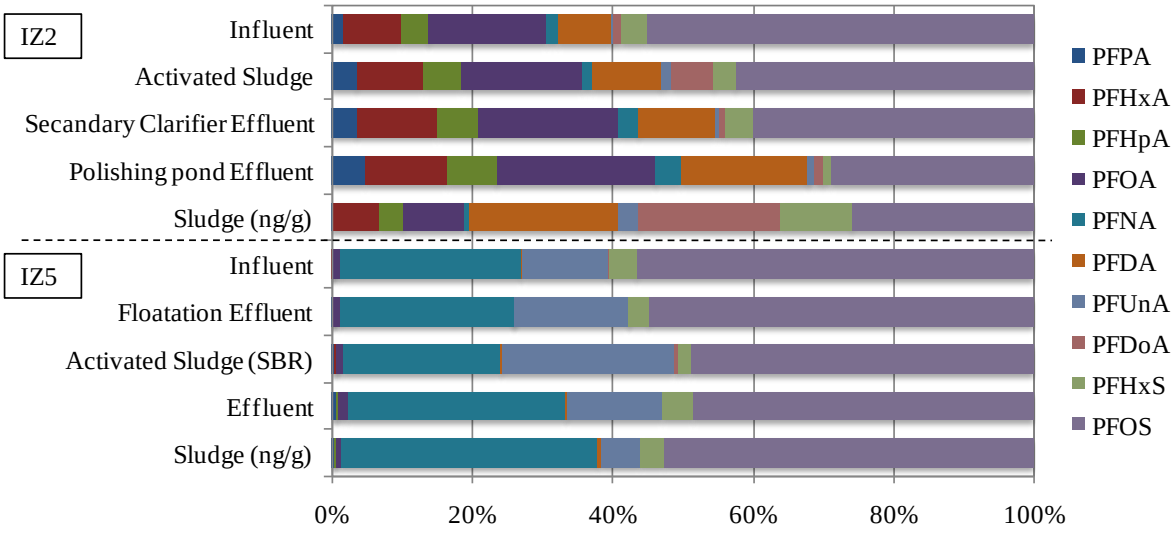


Figure 7.3 Relative abundances of PFCs in IZ2 and IZ5 WWTPs

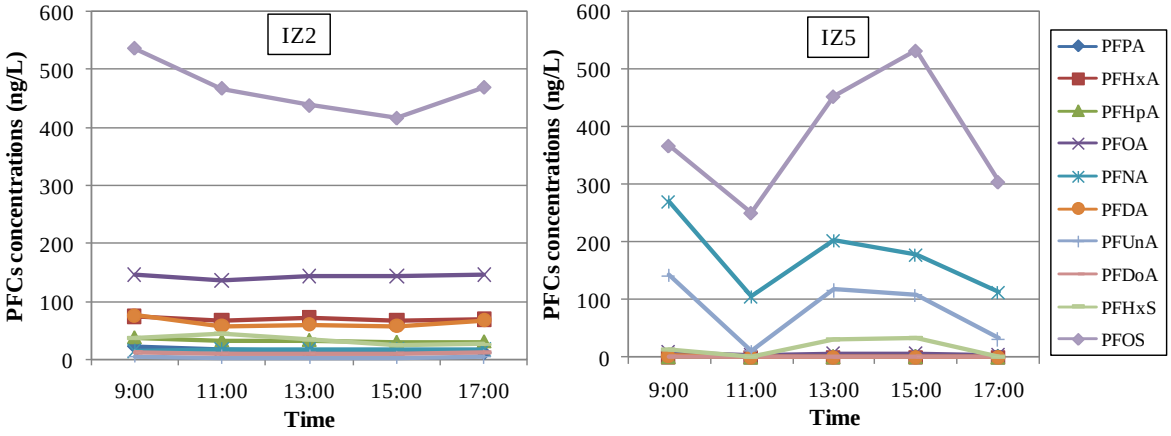


Figure 7.4 Variation of PFCs concentrations in the influent of IZ2 and IZ5 WWTPs

In this chapter, samples were collected five times at 9:00, 11:00, 13:00, 15:00 and 17:00. Figure 7.4 shows the variation of PFCs concentration in the influent of IZ2 and IZ5 WWTPs. PFCs concentrations in IZ2 were slightly fluctuated except PFOS, which was ranged from 416 ng/L to 536 ng/L. The highest concentration was detected at 9:00. The fluctuation of the concentration also caused the variation in the effluent, ranging from 151 ng/L to 225 ng/L. More variation of the PFCs concentration was detected in IZ5. PFOS, PFNA and PFUnA were shown the similar fluctuation in the influent. The ranges of PFOS, PFNA and PFUnA were 250 – 533 ng/L, 107 – 271 ng/L and 10 – 143 ng/L, respectively. The highest concentration of PFNA, and PFUnA were detected at

9:00, while the highest PFOS were detected at15:00. Elevated concentrations of PFOS were found during 13:00 and 15:00 suggests that there might be an industry discharged in either PFOS or precursors to this compound in that period.

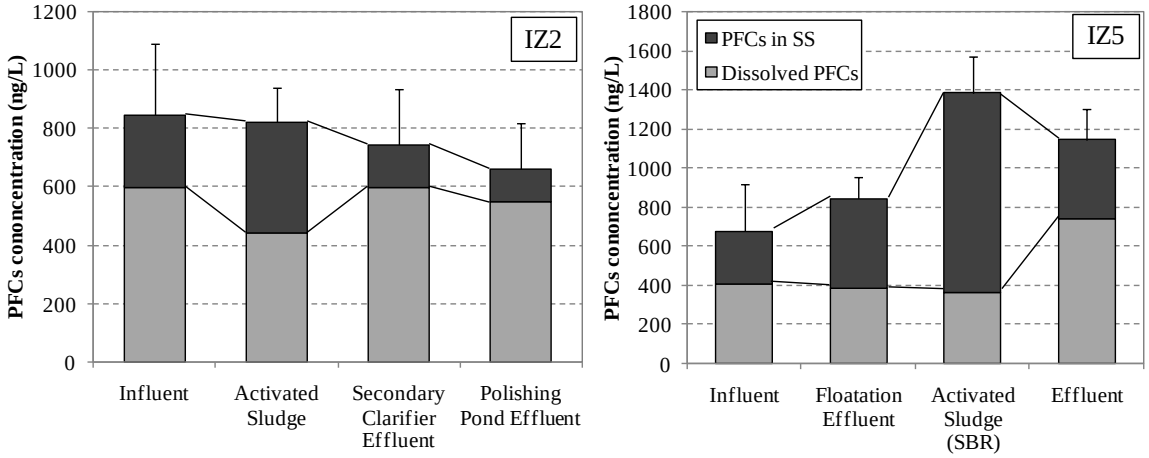


Figure 7.5 Total PFCs concentration during WWTP processes in IZ2 and IZ5

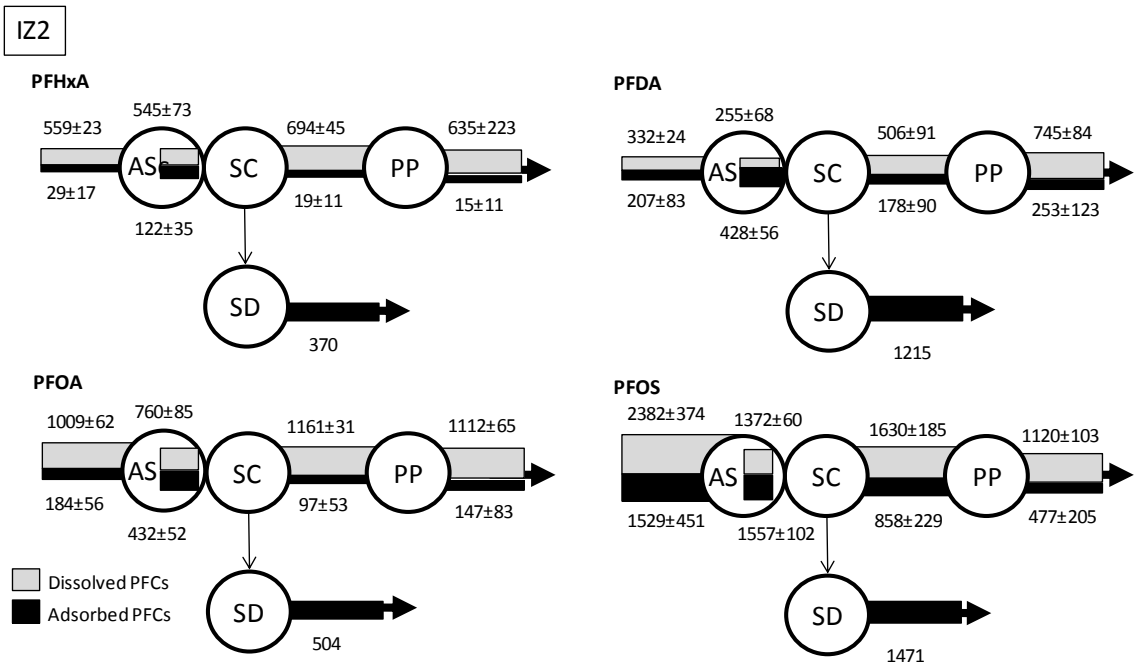
Figure 7.5 shows the average total PFCs concentration in both dissolved and solid phases during WWTP processes in IZ2 and IZ5. In IZ2 WWTPs (Figure 7.1), combined PFCs concentration in both phases was decreasing in each treatment process. PFCs were detected in the influent 848 ng/L. Influent was flow to equalization tank, which mixed with the supernatant from the sludge treatment processes and returned sludge. The PFCs level in the solid phase was increasing in the aeration tank might be from this reason. There might be some degradation of precursors of PFCs that increased dissolved PFCs concentrations in the secondary clarifier. The effluent from secondary clarifier flows to polishing pond, in which similar PFCs level was detected. The efficiency of the treatment process was 22% for all PFCs.

SBR system was used for treating wastewater in IZ5. The flow diagram was shown in Figure 7.1. Total PFCs concentration in combined phases was increasing in each process. However, the concentration in dissolved phase did not increase in flotation process. The additional concentration in SS might come from the return supernatant in the equalization tank similar to IZ2. SBR system is the one tank system that performs aeration and sedimentation in the same tank. Most parts of the sludge remain in the

tank, while only excess sludge discharges to sludge treatment process. This should be the reason that PFCs in SS increased in SBR tank. Similar to IZ2, dissolved PFCs concentration in the effluent was higher than activated sludge that might be some degradation of precursors of PFCs in the process, which were similar to the literatures (Sinclair *et al*., 2006; Schultz *et al*., 2006; Yu *et al*., 2009; Murakami *et al*., 2009). In addition, PFCs in SS decreased by the sedimentation separation. There was the increasing of the concentration in the effluent, indicating the precursors of PFCs have been used in this IZ5.

7.6 PFCs Mass Flow Analysis in Central Wastewater Treatment Plant in Industrial Zones

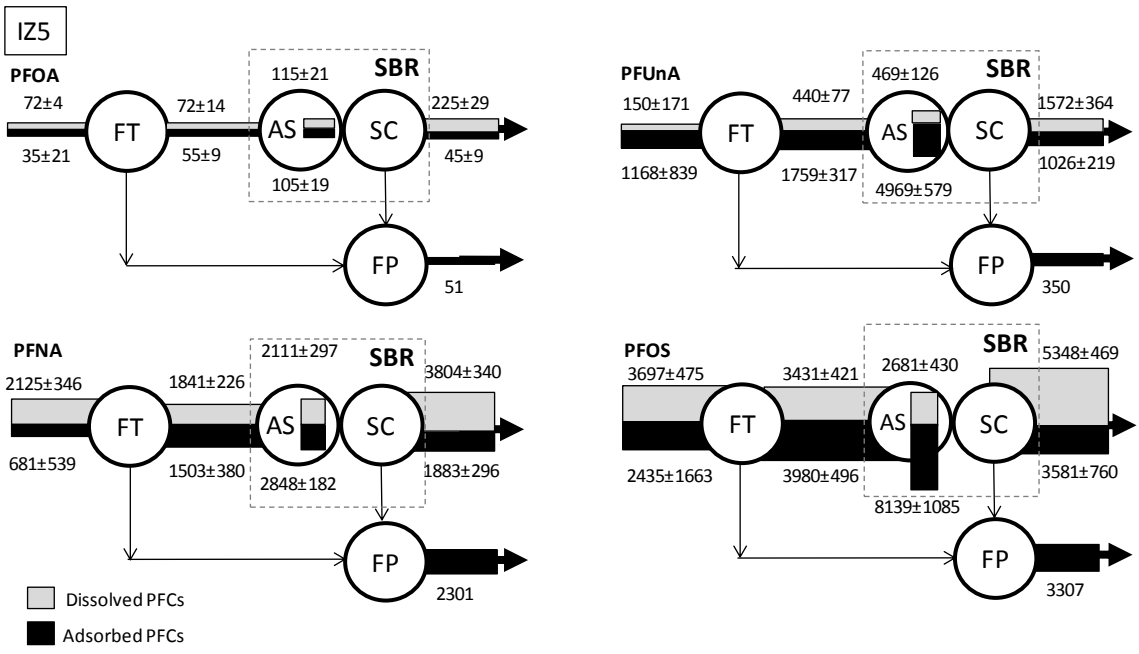
Dominant PFCs in each industrial zone were selected in mass flow analysis. PFHxA, PFOA, PFDA, and PFOS were the predominant compounds in IZ2. PFOA, PFNA, PFUnA, and PFOS were selected for IZ5. Other PFCs were detected with less than ten percent of total PFCs.



Note: AS = Activated Sludge, SC= Secondary Clarifier, PP = Polishing Pond, SD = Sand Drying Bed

Figure 7.6 Mass flows (average mg/d ± standard deviation) for selected PFCs in IZ2

Figure 7.6 shows the mass flow of PFCs in IZ2. PFHxA was entering the process mainly in the aqueous phase and increased in the activated sludge in the solid phase. The mass flow of PFHxA increased 24% after secondary clarifier. PFCs in the SS decreased after sedimentation. Most parts of PFCs in SS were discharged as the sludge cake with the loading of 370 mg/d. The major released of PFHxA was through the dissolved phase with 635 mg/d. Higher loading of PFOA were entering the process (1,193 mg/d). PFOA loading in the dissolved phase increased after activated sludge process by 5%, similar to the previous research in municipal WWTP in U.S.A. (Schultz *et al*., 2006). There was no degradation of PFOA in the polishing pond. PFOA were discharged to the environment through the effluent and sludge with the loading of 1,259 mg/d and 504 mg/d, respectively. PFDA loading were increased during the process with 27% after activated sludge and 46% after polishing ponds, indicating that precursors of PFDA were used in this industrial zone. The highest loading to the treatment plant was PFOS with the loading of 2,382 mg/d and 1,529 mg/d in dissolved and adsorbed phase, respectively. Unlike PFCAs that showed no removal in the treatment process. PFOS were decreased during the treatment processes with 36% in the activated sludge process and 36% in the polishing pond. PFOS were highest in the sludge with 1,471 mg/d.



Note: FT = Floatation, AS = Activated Sludge, SC= Secondary Clarifier, FP = Filter Press

Figure 7.7 Mass flows (average mg/d ± standard deviation) for selected PFCs in IZ5

Figure 7.7 shows the mass flows of PFOA, PFNA, PFUnA, and PFOS in IZ5. Lower PFOA were entering the process in IZ5 with the loading of 107 mg/d. The increment of PFOA loading was found in the effluent, which was 270 mg/d. PFNA was shown the similar result with PFOA in the increasing of the loading during the treatment process. PFNA in the adsorbed phase was also increasing by 176%. Total PFNA released from IZ 5 was 7,988 mg/d. PFUnA was detected in adsorbed phase more than in the dissolved phase. 90% of PFUnA loading was detected in the influent. The predominant in this IZ5 was PFOS. PFOS loading of 6,132 mg/d was entering the SBR process. The increasing of PFOS was also found in this treatment plant differ from IZ2. PFOS was increasing by 45% in dissolved phase and 47% in adsorbed phase. PFOS was the highest found in the sludge with 3,307 mg/d. All of PFCs in this industrial zone were detected higher in the effluent. The precursors should be the major effects of this contamination.

7.7 Summary

Samples were collected from different processes (influent, aeration tank, secondary clarifier effluent, effluent and sludge) every two hour at 9:00, 11:00, 13:00, 15:00, and 17:00 on 2009/1/20 for IZ2 and on 2009/1/22 for IZ5. PFCs were detected in both wastewater and sludge in most samples. PFCs concentration in dissolved phase was higher than PFCs in SS. Higher PFCs in SS were detected only in activated sludge and some influent samples. Total PFCs concentrations in wastewater samples in IZ2 were 847 ng/L in influent and 662 ng/L in effluent in IZ2. Sludge samples from WWTPs contained 1,539 ng/g of total PFCs. PFCs concentrations in IZ2 were slightly fluctuated except PFOS, which was ranged from 416 ng/L to 536 ng/L. The highest concentration was detected at 9:00. IZ5, total PFCs concentration in influent and effluent were 674 ng/L and 1,143 ng/L, respectively. Total PFCs concentration in the sludge was 1,404 ng/g. More variation of the PFCs concentration was detected in IZ5. PFOS, PFNA and PFUnA were shown the similar fluctuation in the influent. The ranges of PFOS, PFNA and PFUnA were 250 – 533 ng/L, 107 – 271 ng/L and 10 – 143 ng/L, respectively.

In IZ2, PFOA loading in the dissolved phase increased after activated sludge process by 5%. There was no degradation of PFOA inside the polishing pond. PFOA were discharged to the environment through the effluent and sludge with the loading of 1,259 mg/d and 504 mg/d, respectively. The highest loading to the treatment plant was PFOS with the loading of 2,382 mg/d and 1,529 mg/d in dissolved and adsorbed phase, respectively. Unlike PFCAs that showed no removal in the treatment process. PFOS were decreased during the treatment processes with 36% in the activated sludge process and 36% in the polishing pond. PFOS were highest in the sludge with 1,471 mg/d. Lower PFOA were entering the process in IZ5 with the loading of 107 mg/d. The increment of PFOA loading was found in the effluent, which was 270 mg/d. PFUnA was detected in adsorbed phase more than in the dissolved phase. 90% of PFUnA loading was detected in the influent. The predominant in this IZ5 was PFOS. The increasing of PFOS was also found in this treatment plant differ from IZ2. PFOS was increasing by 45% in dissolved phase and 47% in adsorbed phase. All of PFCs in this industrial zone were detected higher in the effluent. The precursors should be the major effects of this contamination.

Chapter 8

Conclusions and Recommendations

8.1 Conclusions

Occurrences of PFCs in surface water in the area were identified. PFCs were detected in all samples, indicating that most of the surface water in this area contaminated by PFCs. The samplings were conducted in major rivers, Chao Phraya, Bangpakong and Tachin River. The average combined ten PFCs were 15.10 ng/L and 18.29 ng/L in Chao Phraya and Bangpakong River, respectively. Lower concentration was detected in Tachin River with the total PFCs 7.40 ng/L. PFOS and PFOA were the predominant PFCs in all samples. From three major rivers, the total of 118.6 g/d PFOS and 323.6 g/d PFOA were released daily from the three rivers to the Gulf of Thailand.

Moreover, the survey was also conducted in small rivers, reservoirs, and coastal water around Eastern Thailand. Compare to major rivers, much higher PFCs concentration were detected in this samples. The geometric mean (GM) concentrations of each PFC were ranged from 2.3 to 107.7 ng/L in small rivers, 2.2 to 212.2 ng/L in reservoirs, and 0.8 to 41.1 ng/L in coastal water samples. Rivers and reservoirs were discharged PFCs to the sea, where PFCs could detect in the coastal water. PFOS and PFOA concentration in the coastal water were less than in the river due to the dispersion of PFCs in the sea. Overall, the higher PFCs contaminations were detected in the area of the industrial zones, where might be the source of these compounds. The rivers and reservoirs, which locate in the downstream of the industrial zones, detected PFCs contaminations. The PFCs in rivers and reservoirs were discharged to the Gulf of Thailand, where is the important food source for Thai people and exports

Industrial activities were one of the important sources of PFCs contaminated in the water environment. The industrial zones, where many industries were located, were

selected as the sampling area. Field surveys were conducted in ten industrial zones. The recovery rates of the samples indicated that the matrix interferences were a major concern in PFCs analysis. All PFCs were detected in most samples above *LOQ*. The elevated concentrations were detected in electronics, textile, chemicals and glass making industries. The highest concentration was detected at one of the electronics industries, while the lowest was found in food industry. Total PFCs concentrations in the influent of WWTP were ranged from 39.6 to 3,344.1 ng/L. The elevated concentrations were found in IZ2 and IZ5 accounting for 1,812.6 ng/L and 3,344.1 ng/L, respectively. The major PFCs found in IZ2 were PFOA, PFHxA, PFDA, and PFOS, accounting for 54%, 19%, 9%, and 8% of total PFCs, while in IZ5 only PFOS was the dominant PFCs with 90%. Ten industrial zones released 188.41 g/d of PFCs. All of the treatment processes inside industrial zones were biological processes. Most treatment processes were not effective to remove PFOS and PFOA. However, the result from this study also showed that RO process was effective to remove PFCs in the real scale application. Advanced processes in the IZ5 can remove PFOS and PFOA by 99.3 and 98.5%, respectively.

Repeated samplings were performed in the industrial zones IZ2 and IZ5, where the elevated concentration of PFOS and PFOA, were detected in the first sampling to identify the reproducibility of PFOS and PFOA. Both PFOS and PFOA were detected in most samples in first and second sampling. This provides evidence that PFOS and PFOA are still released into receiving surface waters. Comparing to trend of PFCs in surface water, it can be concluded that the decreasing PFOS and PFOA concentrations in industrial wastewater also had an effect in the concentration in surface water. The influence of industrial discharges was affected not only the rivers and reservoirs but also in the coastal water. The higher ranges of PFCs were also detected in the coastal water, where high range of PFCs detected in the industrial zone nearby.

Due to the problems in industrial wastewater analysis, several options were applied to overcome the analytical problems in analyzing water and wastewater samples by optimizing SPE procedure. Recoveries of PresepC-Agri and Oasis®HLB were identified. The combination of these two cartridges was the better option for analyzing

PFCs in water samples. The optimum flow rate for loading the samples was 5 mL/min for both cartridges. Methanol (2 mL) plus Acetronitrile (2 mL) was the effective way to elute PFCs from the cartridges. The specific solvent percentages to elute each PFCs were identified for both water and industrial wastewater samples. The matrix removal methods by using Envi-Carb and Ultrafilter were effective to remove the matrix in different types of industrial wastewater samples.

Occurrences of PFCs were detected in surface water, which is the source of tap and drinking water for the people in the area. PFCs were also detected in all tap water and drinking water samples. The concentrations of PFCs in the raw water and WTP samples followed the general trends of PFOA > PFOS > PFPA. PFOS and PFOA concentrations in raw water were found 4.29 ng/L and 16.54 ng/L, respectively. The average PFOS and PFOA concentrations in tap water were detected 0.17 and 3.58 ng/L, respectively. Comparing with tap water, PFCs were found much higher concentration in bottled drinking water. The tap water results also showed that PFOS and PFOA were not similarly distributed to all area in the city. In this case, PFOA were detected higher in the western area, while PFOS concentration was quite similar in all areas. In general, it can be concluded that the current treatment process was not completely remove PFCs. Nevertheless, PFCs in particulate phase were effectively removed by the primary sedimentation and rapid sand filtration. Currently, there is no standard or guideline value of PFOS and PFOA in Thailand. However, based on the value reported by New Jersey Department of Environmental Protection (2009), PFOA concentrations in tap water and drinking water found in Bangkok was not expected to cause any health risks.

PFCs mass flows in industrial WWTP were studied. Samples were collected from influent, aeration tank, secondary clarifier effluent, effluent and sludge every two hour (IZ2 and IZ5). Higher PFCs in adsorbed phase were detected only in activated sludge and some influent samples. PFCs concentrations in IZ2 were slightly fluctuated except PFOS, which was ranged from 416 ng/L to 536 ng/L. The highest concentration was detected at 9:00. More variation of the PFCs concentration was detected in IZ5. PFOS, PFNA and PFUnA were shown the similar fluctuation in the influent. The ranges of PFOS, PFNA and PFUnA were 250 – 533 ng/L, 107 – 271 ng/L and 10 – 143 ng/L,

respectively. In IZ2, PFOA loading in the dissolved phase increased after activated sludge process by 5%. There was no degradation of PFOA inside the polishing pond. The highest loading to the treatment plant was PFOS with the loading of 2,382 mg/d and 1,529 mg/d in dissolved and adsorbed phase, respectively. Different from PFCAs that showed no removal in the treatment process. PFOS were decreased during the treatment processes with 36% in the activated sludge process and 36% in the polishing pond. Lower PFOA were entering the process in IZ5 with the loading of 107 mg/d. The predominant in this IZ5 was PFOS. The increasing of PFOS was also found in this treatment plant differ from IZ2. PFOS was increasing by 45% in dissolved phase and 47% in adsorbed phase. All of PFCs in this industrial zone were detected higher in the effluent. The precursors should be the major effects.

8.2 Recommendations

The study results indicated PFCs contamination in surface water, tap water and industrial wastewater from the industrial area. The following are the recommendations.

(1) The fate and behavior of PFCs to the aquatic environment and biota should be identified to evaluate the risk to human through the food chain.
(2) The occurrences of PFCs and precursors in air, rain, and soil samples should be recognized to evaluate the PFCs mass flow in the area.
(3) Toxicity study is needed to set the standards for drinking and tap water.
(4) The risks assessment study to human by the drinking water, tap water, and food pathway is essential.
(5) Research on the treatment of PFCs in different type of industrial wastewater should be done and applied to real scale application.
(6) Occurrences of PFCs and precursors in WTP and WWTP system should parallel identified to evaluate the breakdown of precursors to PFCs.

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